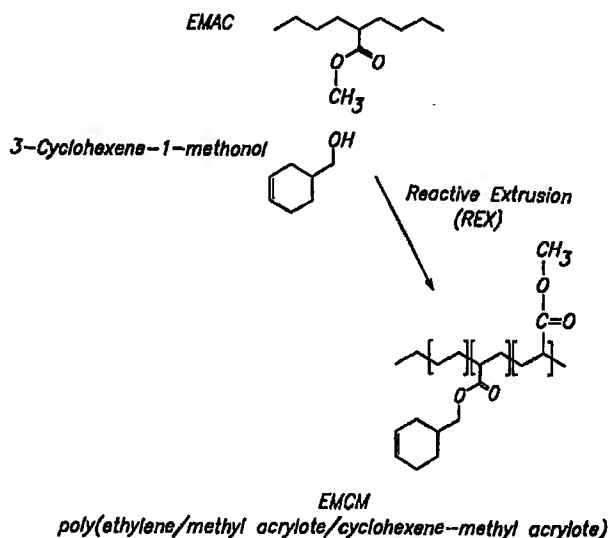




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08K 5/09		A2	(11) International Publication Number: WO 99/48963
			(43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/US99/06379		(74) Agents: HAYMOND, W., Bradley et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).	
(22) International Filing Date: 24 March 1999 (24.03.99)			
(30) Priority Data: 330077 25 March 1998 (25.03.98) NZ 09/127,316 31 July 1998 (31.07.98) US		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(71) Applicants: CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US). SEALED AIR (NZ) LIMITED [NZ/NZ]; Private Bag 3085, Corner Avalon Drive & Foreman Road (NZ).			
(72) Inventors: CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US). CAI, Gangfeng; 335 Glasgow Circle, Danville, CA 94526 (US). DEPREE, Craig; 27 Pembroke Street, Palmerston North (NZ). GALLAND, Mark, Steven; 2806 Chasse Ridge Drive, Orange, TX 77632 (US). GOODRICH, Joseph, L.; 3545 Wilkinson Lane, Lafayette, CA 94549 (US). LEONARD, James, P.; 545 Bret Harte Road, San Rafael, CA 94901 (US). MATTHEWS, Andrew; 106 West Shallowstone Road, Greer, SC 29650 (US). RUSSELL, Kenneth, W.; Route 10, Box 1366, Orange, TX 77630 (US). YANG, Hu; 360 Bellflower Court, San Ramon, CA 94583 (US).		Published Without international search report and to be republished upon receipt of that report.	

(54) Title: OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS



(57) Abstract

An oxygen scavenger composition, for use in or with plastics materials, includes a polymer or oligomer having at least one cyclohexene group or functionality. The composition produces only low levels of volatile or (extractable from a plastics material in which it is incorporated) products as a consequence of oxygen scavenging. A family of polymers containing selected cyclic allylic pendent groups for oxygen scavenging packaging which has minimal organoleptic by-products after oxidation. Multilayer plastic containers for food and beverage packaging which incorporate oxygen scavenging resins which selectively oxidize upon activation without giving off odorous fragments.

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1 OXYGEN SCAVENGERS WITH REDUCED OXIDATION PRODUCTS FOR
2 USE IN PLASTIC FILMS AND BEVERAGE AND FOOD CONTAINERS
3
4

5 Field of the Invention

6 The present invention is directed to oxygen scavengers for use in plastics
7 materials, and in particular plastics films. Emphasis is given to scavengers
8 which produce low or negligible levels of oxidation by-products which may
9 contaminate the head space in a package. This invention also relates to a
10 composition useful in scavenging oxygen from environments containing
11 oxygen-sensitive products, particularly food and beverage products. More
12 specifically, the oxygen scavenging composition includes a polymer having
13 ethylenic unsaturation contained within a cyclic moiety, a transition metal
14 compound and, optionally, a photoinitiator. The present invention also relates
15 to compositions for use in areas such as food packaging, and with minimal
16 effect on odor and taste of packaged contents. The invention preferably uses
17 ethylene acrylate copolymers which are modified with selected cyclic allylic
18 pendent groups for use in oxygen scavenging packaging materials. The
19 present invention also relates to rigid polymeric food or beverage containers
20 comprising polyester such as polyester terephthalate or polyester naphthalate
21 and oxygen scavenging polymer.
22
23
24

25 Background of the Invention
26

27 The majority of plastic films produced are employed in some form of
28 packaging. The present invention is primarily concerned with those films
29 used for applications requiring a low level of oxygen in a package, though
30 may also find other uses.

-2-

1 Limiting the exposure of oxygen-sensitive products to oxygen maintains and
2 enhances the quality and shelf life of many products. For instance, by limiting
3 the oxygen exposure of oxygen-sensitive food products in a packaging
4 system, the quality of the food product can be maintained and spoilage
5 retarded. In addition, such packaging also keeps the product in inventory
6 longer, thereby reducing costs incurred from waste and having to restock.

7
8 In the food packaging industry, several techniques for limiting oxygen
9 exposure have been developed. Common techniques include those where
10 oxygen is consumed within the packaging environment by some means other
11 than the packaged article or the packaging material (e.g., through the use of
12 oxygen scavenging sachets), those where reduced oxygen environments are
13 created in the package (e.g., modified atmosphere packaging (MAP) and
14 vacuum packaging), and those where oxygen is prevented from entering the
15 packaging environment (e.g., barrier films).

16
17 The art dealing with barrier packaging, and the low oxygen or modified
18 packaging of products is relatively well developed. This includes the use of
19 films and inserts containing oxygen scavenging compounds able to extract a
20 majority of any residual oxygen after packaging occurs.

21
22 Oxygen scavenging compounds for use in plastic films are relatively well
23 known. Typically these comprise unsaturated compounds in combination with
24 a transition metal catalyst. In response to some form of initiation—usually
25 exposure to light or radiation—the scavengers react with available oxygen in
26 the package.

27
28 For instance:

29

1 Michael Rooney, "Oxygen scavenging: a novel use of rubber photo-
2 oxidation", *Chemistry and Industry*, March 20, 1982, pp. 197-198, describes
3 the use of ethylenically unsaturated compounds as oxygen scavengers on
4 exposure to light. However, systems describing the use of transition metal
5 catalysts are not described.
6
7 US 4,908,151 to Mitsubishi describes sachets containing unsaturated fatty
8 acid (i.e., an ethylenically unsaturated hydrocarbon) in combination with a
9 transition metal compound in a basic substance. However, there is no
10 description of these materials in the form of a film nor the use of photo-
11 exposure as an initiating mechanism.
12
13 Japanese patent JP5032277 to Kuwa describes the use of radical containing
14 resin layers in packages. The invention comprises an oxidizable polymer
15 whose oxygen scavenging abilities is photoinitiated.
16
17 New Zealand patent application NZ241802 to W R Grace and also NZ243077
18 also to W R Grace, claim oxygen scavenging compositions comprising
19 ethylenically unsaturated hydrocarbons with transition metal catalysts. A wide
20 range of ethylenically unsaturated compounds are discussed in the texts of
21 these specifications though there is no mention of the problems to which the
22 present invention is directed, nor the compounds and products encompassed
23 by the present invention.
24
25 Sachets containing an oxygen scavenging compositions can contain ferrous
26 compositions, which oxidize to their ferric state, unsaturated fatty acid salts on
27 an absorbent, and/or a metal-polyamide complex. See, e.g., U.S. Patent
28 Nos. 4,908,151 and 5,194,478. The disadvantages of sachets include the
29 need for additional packaging steps (to add the sachet to the package), the

1 potential for contamination of the packaged article should the sachet break
2 and the danger of ingestion by a consumer.

3

4 Oxygen scavenging materials also have been incorporated directly into the
5 packaging structure. This technique (hereinafter referred to as "active oxygen
6 barrier") can provide a uniform scavenging effect throughout the package and
7 can provide a means of intercepting and scavenging oxygen as it passes
8 through the walls of a package, thereby maintaining the lowest possible
9 oxygen level throughout the package. Active oxygen barriers have been
10 formed by incorporating inorganic powders and/or salts as part of the
11 package. See, e.g., U.S. Patent Nos. 5,153,038, 5,116,660, 5,143,769, and
12 5,089,323. However, incorporation of such powders and/or salts can degrade
13 the transparency and mechanical properties (e.g., tear strength) of the
14 packaging material and can complicate processing, especially where thin
15 films are desired. Also, these compounds as well as their oxidation products
16 can be absorbed by food in the container, which can result in the food product
17 failing to meet governmental standards for human consumption.

18

19 EP 0 519 616 discloses an oxygen scavenging composition that includes a
20 blend of an epoxide, a first polymeric component grafted with an unsaturated
21 carboxylic anhydride and/or acid, a second polymeric component including
22 OH, SH, or NHR^2 groups where R^2 is H, C_1 - C_3 alkyl, or substituted C_1 - C_3 alkyl
23 moiety, and a metal salt capable of catalyzing the reaction between oxygen
24 and the second polymeric component. The first polymeric component is
25 present in an amount sufficient to ensure that the blend is non-phase
26 separated. A blend of polymers is utilized to obtain oxygen scavenging, and
27 the second polymeric component is preferably a (co)polyamide such as
28 MXD6.

29

1 Another type of active oxygen barrier is illustrated in EP-A-0 301 719,
2 EP-A-0 380 319, PCT Publication No. WO 90/00578, and PCT Publication
3 No. WO 90/00504. See also U.S. Patent Nos. 5,021,515 5,194,478, and
4 5,159,005. The disclosed oxygen scavenger includes polyamide-transition
5 metal catalyst compositions. Through catalyzed scavenging by the
6 polyamide, the package wall regulates the amount of oxygen reaching the
7 interior of the package. However, the onset of useful oxygen scavenging (i.e.,
8 up to about $5.8 \times 10^{-5} \text{ cm}^3/\text{m}^2 \cdot 24$ hours at ambient conditions) can take as
9 long as 30 days to occur. Therefore, this technique is not acceptable for
10 many applications. Further, polyamides typically are incompatible with many
11 thermoplastic polymers commonly used to make flexible packaging materials
12 (e.g., ethylene/vinyl acetate copolymers, low density polyethylene, etc.) or,
13 when used by themselves, are difficult to process and result in inappropriately
14 stiff structures.

15
16 Oxygen scavenging compositions that include transition metal catalysts and
17 ethylenically unsaturated hydrocarbon polymers which have an ethylenic
18 double bond content of from 0.01 to 10 equivalents per 100 grams of polymer
19 are disclosed in U.S. Patent No. 5,399,289. Various conventional
20 homopolymers, copolymers, and polymer blends are disclosed. Because
21 these polymers are amorphous, they can be difficult to blend and process
22 with film-forming semicrystalline polymers conventionally used to make
23 flexible packaging materials.

24
25 The use of a transition metal and a photoinitiator to facilitate initiation of
26 effective scavenging activity of ethylenically unsaturated compounds is taught
27 in U.S. Patent No. 5,211, 875, which is incorporated herein by reference as if
28 set forth in full.

29

1 PCT Publication Nos. WO 95/02616 and WO 96/40799 disclose a scavenger
2 composition that includes a transition metal salt and a copolymer (of ethylene
3 and a vinyl monomer) having ether, amino, carboxylic acid, ester, or amide
4 functionalities pendent therefrom. Although these compositions can provide
5 oxygen scavenging activity, the particular advantages of having ethylenic
6 unsaturation contained within a cyclic moiety are not disclosed. Because the
7 compositions of this invention are significantly cleaner than those described in
8 the prior art, they do not require the use of high levels of adjuncts to absorb
9 the undesirable byproducts. Such absorbent additives are known in the art,
10 for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well known in
11 the art that such additives (zeolites and silicas) adversely affect the haze and
12 clarity of packaging structures.

13

14 PCT Application WO 96/40799 from Chevron describes the use of a variety of
15 ethylenic materials with benzylic, allylic or ether containing side chains. Some
16 of these materials may be prepared by esterification or transesterification of a
17 polymer melt. The use of pendent cyclic groups containing allylic
18 unsaturation is generally referred to, but there is only one such example,
19 wherein Nopol, a bicyclic alcohol, is used in a transesterification reaction and
20 oxygen absorbing films are formulated from the product. There is no
21 reference to the benefits of cyclic allylic compounds as described in this
22 invention i.e., on oxidation they produce very low levels of oxidation
23 byproducts when compared to comparable linear allylic systems. Because of
24 its bicyclic nature, Nopol is not expected to produce these benefits.

25

26 While the prior art compounds may effectively scavenge oxygen they
27 introduce other problems into packaging. For instance, in summary the prior
28 art incorporates into film structures compounds which are ethylenically
29 unsaturated but which often cleave as a consequence of the reactions of the
30 oxygen scavenging process. For example, films containing unsaturated

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1 compounds such as squalene or vegetable oils produce large amounts of
2 volatile aldehydes and ketones upon oxidation. Unfortunately, many of these
3 volatile compounds are not contained within the film structure and find their
4 way into the head space of the package. Here they can represent more of a
5 problem than the oxygen which they have replaced and have the potential to
6 contaminate comestible products.

7

8 This problem represents a significant problem yet has been downplayed or
9 overlooked by the published prior art. As a consequence, those searching
10 the prior art for a solution to this problem find no answer—the art appears to
11 be directed primarily along a narrow track of improving on scavenging
12 efficiencies, or physical properties of scavenging films, rather than
13 recognizing or addressing other associated problems.

14

15 Accordingly the present invention seeks to address the problems associated
16 with scission products of oxygen scavengers, and seeks also to provide a
17 group of compounds and substances (as well as films and plastics materials
18 including same) which have an advantage over the prior art in terms of
19 reduced quantities of scission products.

20

21 Ideally, a polymeric material for use in an oxygen scavenging composition
22 should exhibit good processing characteristics, be able to be formed into
23 useful packaging materials or have high compatibility with those polymers
24 commonly used to make packaging materials, and not produce byproducts
25 which detract from the color, taste, or odor of the packaged product. It has
26 been found that when the ethylenic unsaturation is contained within a cyclic
27 group, substantially fewer and less byproducts are produced upon oxidation
28 as compared to analogous non-cyclic materials. Optimally, a packaging

1 material formed from such a composition can retain its physical properties
2 after significant oxygen scavenging.

3

4

5 New polymer compositions having properties that are particularly tailored for
6 specific applications are required in response to more specific and
7 sophisticated end uses. It can be difficult to make these compositions directly
8 by polymerization from monomers or via solution esterification or
9 transesterification, but manufacturing them in melt mixing equipment such as
10 an extruder has provided an efficient, economical and viable means to supply
11 increasingly complex polymers to meet the needs in specialized markets.

12 It is well known that regulating the exposure of oxygen-sensitive products to
13 oxygen maintains and enhances the quality and "shelf-life" of the product.
14 For instance, by limiting the exposure of oxygen sensitive food products to
15 oxygen in a packaging system, the quality or freshness of food is maintained,
16 spoilage reduced and the food shelf life extended. In the food packaging
17 industry, several means for regulating oxygen exposure have already been
18 developed. These means include modified atmosphere packaging (MAP) and
19 oxygen barrier film packaging.

20 One method currently being used is "active packaging", whereby the package
21 containing the food product has been modified in some manner to regulate
22 the food's exposure to oxygen. One form of active packaging uses oxygen-
23 scavenging sachets which contain a composition which scavenges the
24 oxygen through oxidation reactions. One type of sachet contains iron-based
25 compositions which oxidize to their ferric states. Another type of sachet
26 contains unsaturated fatty acid salts on a particulate adsorbent. Yet another
27 sachet contains metal/polyamide complex. However, one disadvantage of

1 sachets is the need for additional packaging operations to add the sachet to
2 each package. A further disadvantage arising from the iron-based sachets is
3 that certain atmospheric conditions (e.g., high humidity, low CO₂ level) in the
4 package are sometimes required in order for scavenging to occur at an
5 adequate rate. Further, the sachets can present a problem to consumers if
6 accidentally ingested.

7 Another means for regulating exposure of a packaged product to oxygen
8 involves incorporating an oxygen scavenger into the packaging structure
9 itself. A more uniform scavenging effect through the package is achieved by
10 incorporating the scavenging material in the package instead of adding a
11 separate scavenger structure (e.g., a sachet) to the package. This may be
12 especially important where there is restricted airflow inside the package. In
13 addition, incorporating the oxygen scavenger into the package structure
14 provides a means of intercepting and scavenging oxygen as it permeates the
15 walls of the package (herein referred to as an "active oxygen barrier"),
16 thereby maintaining the lowest possible oxygen level in the package.

17 One attempt to prepare an oxygen-scavenging wall involves the incorporation
18 of inorganic powders and/or salts. However, incorporation of these powders
19 and/or salts causes reduction of the wall's optical transparency, discoloration
20 after oxidation, and reduced mechanical properties such as tear strength. In
21 addition, these compounds can lead to processing difficulties, especially
22 when fabricating thin films. The oxidation products may migrate into food at
23 levels which would not be regarded as safe or can impart unacceptable taste
24 or smell to food.

25 An oxygen-scavenging composition comprising a blend of a first polymeric
26 component comprising a polyolefin is known, the first polymeric component
27 having been grafted with an unsaturated carboxylic anhydride or an
28 unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a

1 second polymeric component having -OH, -SH, or -NHR² groups where R² is
2 H, C₁-C₃ alkyl, substituted C₁-C₃ alkyl; and a catalytical amount of metal salt
3 capable of catalyzing the reaction between oxygen and the second polymeric
4 component, the polyolefin being present in an amount sufficient so that the
5 blend is not phase-separated. A blend of polymers is utilized to obtain
6 oxygen scavenging, and the second polymeric component is preferably a
7 polyamide or a copolyamide such as the copolymer of m-xylylene-diamine
8 and adipic acid (MXD6).

9 Some oxygen scavenging systems produce an oxygen-scavenging wall. This
10 is done by incorporating a metal catalyst-polyamide oxygen scavenging
11 system into the package wall. Through catalyzed oxidation of the polyamide,
12 the package wall regulates the amount of oxygen which reaches the interior
13 volume of the package (active oxygen barrier) and has been reported to have
14 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc)
15 oxygen per square meter per day at ambient conditions. However, this
16 system suffers from significant disadvantages.

17 One particularly limiting disadvantage of polyamide/catalyst materials can be
18 a low oxygen scavenging rate. Adding these materials to a high-barrier
19 package containing air can produce a package which is not generally suitable
20 for creating an internal oxygen level of less than 0.1% within seven days at
21 storage temperatures, as is typically required for headspace oxygen
22 scavenging applications.

23 There are also disadvantages to having the oxygen-scavenging groups in the
24 backbone or network structure in this type of polyamide polymer. The basic
25 polymer structure can be degraded and weakened upon reaction with oxygen.
26 This can adversely affect physical properties such as tensile or impact
27 strength of the polymer. The degradation of the backbone or network of the

1 polymer can further increase the permeability of the polymer to those
2 materials sought to be excluded, such as oxygen.

3 Moreover, polyamides previously used in oxygen scavenging materials, such
4 as MXD6, are typically incompatible with thermoplastic polymers used in most
5 flexible packaging walls, such as ethylene-vinyl acetate copolymers and low
6 density polyethylene. Even further, when such polyamides are used by
7 themselves to make a flexible package wall, they may result in inappropriately
8 stiff structures. They also incur processing difficulties and higher costs when
9 compared with the costs of thermoplastic polymers typically used to make
10 flexible packaging. Even further, they are difficult to heat seal. Thus, all of
11 these are factors to consider when selecting materials for packages,
12 especially multi-layer flexible packages and when selecting systems for
13 reducing oxygen exposure of packaged products.

14 Another approach to scavenging oxygen is an oxygen-scavenging
15 composition comprising an ethylenically unsaturated hydrocarbon and a
16 transition metal catalyst. Ethylenically unsaturated compounds such as
17 squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen
18 scavenging compositions, and ethylenically saturated compounds such as
19 polyethylene and ethylene copolymers are used as diluents. Compositions
20 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically
21 have an oily texture as the compound migrates toward the surface of the
22 material. Further, polymer chains which are ethylenically unsaturated in the
23 backbone would be expected to degrade upon scavenging oxygen,
24 weakening the polymer due to polymer backbone breakage, and generating a
25 variety of off-odor/off-taste by-products.

26 Other oxidizable polymers recognized in the art include "highly active"
27 oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate),
28 EMBZ, and poly(ethylene-methyl acrylate-tetrahydrofurfuryl acrylate), EMTF,

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1 as well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Although
2 effective as oxygen scavengers, these polymers have the drawback of giving
3 off large amounts of volatile by-products and/or strong odors after oxygen
4 scavenging.

5 Also known are oxygen-scavenging compositions which comprise a transition-
6 metal salt and a compound having an ethylenic backbone and having allylic
7 pendent or terminal moieties which contain a carbon atom that can form a
8 free radical that is resonance-stabilized by an adjacent group. Such a
9 polymer needs to contain a sufficient amount and type of transition metal salt
10 to promote oxygen scavenging by the polymer when the polymer is exposed
11 to an oxygen-containing fluid such as air. Although effective as oxygen
12 scavengers, upon oxidation, we have found that allylic pendent groups on an
13 ethylenic backbone tend to generate considerable amounts of organic
14 fragments. We believe this is a result of oxidative cleavage. We believe
15 these fragments can interfere with the use of allylic pendent groups as
16 oxygen scavengers in food packaging.

17 Multilayer rigid container structures, which utilize an oxygen scavenging
18 composition, are known. In the container wall, base polymers such as
19 polyethylene terephthalate have been used along with an oxygen scavenger.
20 The resulting multilayer package wall includes at least an oxygen scavenger
21 core layer as well as inner and outer layers having high oxygen barrier
22 qualities. The oxygen scavenger core layer is a combination of at least an
23 oxygen scavenging polymer with post consumer-polyethylene terephthalate
24 (PC-PET). The inner and outer layers include at least oxygen barrier quality
25 PET.

26

27 Furthermore, multilayered plastic bottles having oxygen scavenging capacity
28 sufficient to maintain substantially zero or near zero presence of oxygen in

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1 the bottle cavity under specified storage conditions have also been disclosed.
2 The multilayered bottle wall has at least three layers. The inner and outer
3 layers are PET or another bottling polyester, which define the bottle cavity
4 and the outside skin of the bottle respectively. Between the inner and outer
5 layers is an oxygen scavenging copolyester layer.

6
7 Condensation copolymers used for making bottles with polyester such as
8 PET or polyethylene naphthalate (PEN) have also been disclosed. The
9 condensation copolymers comprise predominantly polyester segments and
10 an oxygen scavenging amount of polyolefin oligomer segments. The
11 copolymers are preferably formed by transesterification during reactive
12 extrusion and typically comprise about 0.5 to about 12 wt. % of polyolefin
13 oligomer segments. In a preferred embodiment, a bottle is provided having a
14 multilayer wall of at least three layers. The outer and inner layers are of
15 unmodified PET and the oxygen scavenging layer in between the outer and
16 inner layer is made of the condensation copolymers described above having
17 an oxygen scavenging amount of polyolefin oligomers.

18
19 A transparent oxygen-scavenging article for packaging oxygen sensitive
20 products is also known, the oxygen-scavenging article having a multilayered
21 wall including at least three layers, an inner and outer layer of biaxially-
22 oriented aromatic polyester polymers such as PET or PEN and an oxygen-
23 scavenging aromatic ester polymer compatible with the polyester polymer.
24 The oxygen-scavenging aromatic ester polymer must include ketone carbonyl
25 groups to provide the oxygen-scavenging functionality and aromatic and ester
26 groups for compatibility with the polyester.

27
28 PET containers have been disclosed that have a container wall of stretched
29 plastic material with high oxygen barrier properties and an activating metal
30 incorporated into the plastic material. The plastic material is PET in admixture

1 with a polyamide and the metal is either added to the mixture or contained in
2 one or both of the polymers.

3

4 A container containing at least one layer containing a plastics material and
5 ions of at least one metal has also been disclosed. The plastics material in
6 the layer consists of at least a partially split or degraded polyamide which has
7 increased sensitivity to reaction with oxygen in the presence of metal thus
8 giving the layer improved oxygen barrier properties.

9

10 A container has been disclosed with a wall having high oxygen barrier
11 properties comprising a molded polymer composition, the composition
12 comprising a granular mixture of (1) a first polymer providing essential
13 strength for the container wall and (2) an active component comprising a
14 metal compound capable of scavenging oxygen and consisting essentially of
15 a metal ion having complexing properties and a polymer to which said metal
16 ion is combined as a metal complex in the molded polymer composition of
17 said wall to scavenge oxygen. There is also disclosed a method of producing
18 the polymer composition which can be molded into containers, the method
19 being to treat a polymer with a metal compound dissolved or slurried in a
20 volatile solvent composition during refluxing conditions for obtaining the active
21 component having capacity to scavenge oxygen.

22

23 An article has been disclosed with oxygen barrier properties comprising at
24 least partly a molded polymer composition formed by melting granules of the
25 composition and molding the melted composition to produce the article. The
26 composition comprises a granular mixture of (1) a first polymer composition
27 providing strength for the article and (2) a second polymer composition
28 compatible with the first polymer composition. The second polymer
29 composition is obtainable by reacting a polyamide or copolyamide with a
30 solution of a transition metal compound in a volatile solvent under refluxing

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1 conditions. The polymer of the first polymer composition can be any polymer
2 and the metal of the metal compound reacted with the polyamide or
3 copolyamide can be any transition metal. The amount of metal in the second
4 polymer composition is at least 500 ppm.

5

6 A polymer material having increased sensitivity to reaction with oxygen has
7 also been disclosed, the polymer material comprising a polyamide, which has
8 been reacted with a nucleophilic reagent and possibly an activator. The
9 nucleophilic reagent is selected from the group consisting of compounds
10 containing at least one hydroxyl group, compounds containing at least one
11 alkoxide group, phosphate compounds, pyrophosphate compounds,
12 polyphosphate compounds, salts of organic acids and a copolymer of vinyl
13 alcohol and ethylene. The activator is in the form of a hydrogen donor. A
14 process is also disclosed for producing the polymer material, which has
15 increased sensitivity of reaction with oxygen. In the process, a polyamide
16 reacts with the nucleophilic reagent under such conditions that the polymer
17 material is obtained.

18

19 Such polymeric containers of PET, PEN and/or polyamide as described
20 above utilize oxidizable components to react with and decrease the amount of
21 oxygen in contact with oxygen sensitive materials packaged in containers. All
22 of these oxidizable materials have the disadvantage of imparting unpleasant
23 odor and/or taste to the packaged materials because of the byproducts given
24 off during the oxidation of the oxidizable materials. Another problem is the
25 uncontrolled oxidation fragmentation from the polymer backbone which leads
26 to chain secession, thus weakening the physical integrity of the multilayer
27 container structures.

28

29

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1 The present invention solves many of the problems of the prior art, especially
2 with an oxygen scavenging packaging material incorporating polymers
3 comprising cyclic allylic (olefinic) pendent groups which produce little or no
4 migration of oxidation by-products adversely affecting odor or taste, thus
5 minimizing organoleptic problems in food packaging. This is because the
6 cyclic allylic structures are less likely to fragment or cleave after oxidation
7 than the conventional open chain allylic (olefinic) groups used in oxygen
8 scavenging packaging material.

9
10 Such polymeric containers of PET, PEN and/or polyamide as described
11 above utilize oxidizable components to react with and decrease the amount of
12 oxygen in contact with oxygen sensitive materials packaged in containers. All
13 of these oxidizable materials have the disadvantage of imparting unpleasant
14 odor and/or taste to the packaged materials because of the byproducts given
15 off during the oxidation of the oxidizable materials. Another problem is the
16 uncontrolled oxidation fragmentation from the polymer backbone which leads
17 to chain secession, thus weakening the physical integrity of the multilayer
18 container structures.

19
20 In contrast, the present invention achieves a rigid beverage and food
21 container comprising PET and/or PEN, the container incorporating an oxygen
22 scavenging component of cyclic olefin which does not give off odor and or
23 taste as a result of its oxygen scavenging function. The oxidation also does
24 not cause a change in molecular weight. This is because the cyclic olefin
25 oxygen scavenging component does not fragment as it oxidizes, thus
26 avoiding the problem of imparting oxidation byproducts to the packaged
27 material while maintaining the structural integrity.

28

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1 It is an object of the present invention to address the foregoing problems or at
2 least to provide the public with a useful choice.

3

4 Further aspects and advantages of the present invention will become
5 apparent from the ensuing description, which is given by way of example
6 only.

7

8 SUMMARY OF INVENTION

9

10 According to one aspect of the present invention, there is provided an oxygen
11 scavenger for use in or with plastics materials, said scavenger comprising or
12 including a polymer or oligomer having at least one cyclohexene group or
13 functionality.

14

15 According to another aspect of the present invention, there is provided an
16 oxygen scavenger, substantially as described above, which produces only
17 low levels of volatile or extractable (from a plastics material in which it is
18 incorporated) products as a consequence of oxygen scavenging.

19

20 According to another aspect of the present invention there is provided an
21 oxygen scavenger, substantially as described above, which is substantially
22 stable with respect to reaction with oxygen until triggered by an external
23 event.

24

25 According to another aspect of the present invention, there is provided an
26 oxygen scavenger, substantially as described above, wherein the external
27 event is irradiation by electromagnetic radiation.

28

29 According to a further aspect of the present invention, there is provided an
30 oxygen scavenging composition, including an oxygen scavenger,

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1 substantially as described above, which includes one or more trigger
2 enhancing components making the scavenger susceptible to triggering from
3 an external event.

4

5 According to another aspect of the present invention, there is provided an
6 oxygen scavenging composition, substantially as described above, wherein a
7 trigger-enhancing component may be benzophenone or substituted
8 derivatives thereof.

9

10 According to another aspect of the present invention, there is provided an
11 oxygen scavenging composition, substantially as described above, which
12 includes the presence of one or more catalysts for the scavenging process.

13

14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, substantially as described above, in which a
16 catalyst may be a transition metal salt, compound or complex.

17

18 According to another aspect of the present invention, there is provided an
19 oxygen scavenger or oxygen scavenging composition, substantially as
20 described above, which is in the form of a plastics resin.

21

22 According to another aspect of the present invention, there is provided an
23 oxygen scavenger or oxygen scavenging composition, substantially as
24 described above, in which the plastics resin is a resin suitable for use in the
25 manufacture of plastic films.

26

27 According to another aspect of the present invention, there is provided an
28 oxygen scavenger or oxygen scavenging composition, substantially as
29 described above, in which the plastic resin is a polyester resin.

30

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition, substantially as
3 described above, when present in a plastics film or layer thereof.

4

5 According to another aspect of the present invention, there is provided an
6 oxygen scavenger or oxygen scavenging composition, substantially as
7 described above, when used as a polymeric material of a plastics film, a layer
8 thereof, and/or a coating thereof, or in a plastics material.

9

10 According to another aspect of the present invention, there is provided an
11 oxygen scavenger or oxygen scavenging composition, substantially as
12 described above, when dispersed throughout a plastics film, a layer thereof,
13 and/or a coating thereon, or in a plastics material.

14

15 According to a further aspect of the present invention, there is provided an
16 oxygen scavenger or oxygen scavenging composition, substantially as
17 described above, in which the anhydride comprises 1,2,3,6-tetrahydrophthalic
18 anhydride or tetrahydrophthalic anhydride monomer derivable from
19 butadiene.

20

21 According to a further aspect of the present invention, there is provided an
22 oxygen scavenger or oxygen scavenging composition prepared from the
23 reaction of a tetrahydrobenzyl alcohol with one or more compounds having
24 one or more of the following functionalities: carboxylic acid, acid halide, ester,
25 anhydride, and isocyanate.

26

27 According to another aspect of the present invention, there is provided an
28 oxygen scavenger or oxygen scavenging composition, substantially as
29 described above, in which the alcohol comprises tetrahydrobenzyl alcohol.

30

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition, substantially as
3 described above, in the compounds with which the alcohol is reacted may
4 include a styrene maleic anhydride copolymer, and/or a polyfunctional
5 isocyanate.

6

7 According to another aspect of the present invention, there is provided an
8 oxygen scavenger or oxygen scavenging composition, prepared from a
9 cyclohexene dimethanol compound.

10

11 According to another aspect of the present invention, there is provided an
12 oxygen scavenging polymer including at least one pendant cyclohexene
13 group prepared by a reactive extrusion process.

14

15 According to a further aspect of the present invention, there is provided an
16 oxygen scavenger or oxygen scavenging polymer, substantially as described
17 above, in which the reactive extrusion process comprises an esterification or
18 transesterification step. Suitable catalyst include acids, bases and
19 organometallic compounds such as the titanium alkoxides.

20

21 According to another aspect of the present invention, there is provided an
22 oxygen scavenger or oxygen scavenging polymer prepared by a route
23 including a cyclohexene anhydride.

24

25 According to another aspect of the present invention, there is provided an
26 oxygen scavenger or oxygen scavenging polymer prepared by a route
27 including the reaction of a diene monomer, or hydroxy containing monomer,
28 with a cyclic anhydride.

29

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging polymer, substantially as described
3 above, in which the cyclic anhydride is a maleic anhydride.

4

5 According to a further aspect of the present invention, there is provided an
6 oxygen scavenger including a pendant cyclic alkene group prepared via a
7 method including a Diels Alder addition reaction.

8

9 According to another aspect of the present invention, there is provided an
10 oxygen scavenger, substantially as described above, in which the preferred
11 dienes for use in the Diels Alder reaction is substituted and/or unsubstituted
12 1,3 butadiene.

13 According to another aspect of the present invention, there is provided an
14 oxygen scavenger, substantially as described above, in which the preferred
15 dienophile for use in the Diels Alder reaction include unsaturated acids,
16 anhydrides, and esters.

17

18 According to another aspect of the present invention, there is provided an
19 oxygen scavenger, substantially as described above, in which the cyclic
20 alkene is cyclohexene.

21

22 In other aspects, the present invention provides an article which include at
23 least one layer formed from a blend that includes the foregoing composition
24 as well as a method of scavenging oxygen in which a packaging article, at
25 least one layer of which is formed from a blend that includes the foregoing
26 composition, is exposed to actinic or e-beam radiation so as to activate the
27 composition.

28

1 According to a further aspect of the present invention, there is provided an
2 oxygen scavenger or oxygen scavenging composition prepared from a
3 tetrahydrophthalic anhydride and a polymer or lower molecular weight
4 compound containing at least one amine group.

5

6 According to a further aspect of the present invention, there is provided an
7 oxygen scavenger or oxygen scavenging composition prepared from
8 diglycidyltetrahydrophthalate.

9 According to a further aspect of the present invention, there is provided an
10 oxygen scavenger or oxygen scavenging composition prepared from the
11 reaction of tetrahydrobenzyl alcohol, methyl or dimethyl substituted
12 tetrahydrobenzyl alcohol with one or more compounds having one or more of
13 the following functionalities: carboxylic acid, acid halide, ester, anhydride,
14 epoxide and isocyanate.

15

16 According to a further aspect of the present invention, there is provided an
17 oxygen scavenger or oxygen scavenging composition, substantially as
18 described above, in which a tetrahydrobenzyl alcohol or substituted
19 tetrahydrobenzyl alcohol reacts with one or more of the following materials:

20

21 ethylene (meth)acrylic acid and other acid containing polymers and acid
22 containing lower molecular weight materials;

23

24 styrene maleic anhydride copolymers; alpha olefin maleic anhydride
25 copolymers such as octadecene maleic anhydride; ethylene and ethylene
26 alpha olefin maleic anhydride terpolymers; ethylene alkyl (meth) acrylate
27 maleic anhydride terpolymers and other like anhydride containing polymers or
28 anhydride containing lower molecular weight materials;

29

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1 polymeric or lower molecular weight materials containing acid halide
2 functionality such as poly acryloyl chloride;

3

4 ethylene alkyl (meth)acrylate copolymers and terpolymers and alternative
5 polymers or lower molecular weight materials containing lower alkyl ester
6 functionality;

7

8 epoxy resins;

9

10 isocyanate functional material such as prepolymers and oligomers derived
11 from the common diisocyanates such as MDI, TDI and the like.

12

13 According to a further aspect of the present invention, there is provided an
14 oxygen scavenger or oxygen scavenging composition prepared from a
15 dihydroxy cyclohexene compound. For example, 3 Cyclohexene-1,1-
16 dimethanol or its substituted derivatives may be used to prepare polyurethane
17 and polyester resins.

18

19 According to a further aspect of the present invention, there is provided an
20 oxygen scavenger or oxygen absorbing composition prepared from a
21 cyclohexene carboxylic acid. Such materials may be prepared from acrylic
22 acid and substituted and unsubstituted butadienes. A typical example would
23 be tetrahydrobenzoic acid, derived from acrylic acid and butadiene. This may
24 be reacted with the following materials:

25

26 hydroxyl functional materials such as poly(vinyl alcohol) and polyethylene-
27 vinyl alcohol, hydroxyl functional oligomers such as poly(ethylene glycol), the
28 polyester polyols and other lower molecular weight hydroxyl functional
29 materials;

30

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1 amine functional polymers and lower molecular weight compounds;

2

3 polyvalent metal ions.

4

5 According to a further aspect of the present invention, there is provided an
6 oxygen scavenger prepared from a cyclohexene functional acid chloride.

7 Example 9 utilizes 3-cyclohexene-1-carbonyl chloride.

8

9 According to a further aspect of the present invention, there is provided an
10 oxygen scavenger or oxygen scavenging composition prepared from
11 tetrahydrobenzaldehyde and its substituted derivatives. These may be
12 prepared from reaction of butadiene or the methyl substituted butadienes with
13 acrolein.

14

15 The tetrahydrobenzaldehydes may be reacted with hydroxyl functional
16 polymers such as poly(vinyl alcohol) and polyethylene-vinyl alcohol to form
17 polyvinyl acetals.

18

19 The following definitions apply herein throughout unless a contrary intention is
20 expressly indicated:

21

22 "polymer" means the polymerization product of one or more monomers and
23 includes homopolymers, as well as copolymers;

24 "copolymer" means the polymerization product of two or more kinds of
25 monomers;

26

27 "(meth)acrylate" means acrylate or methacrylate;

28

29 "photoinitiator" means a substance which, when activated by actinic radiation,
30 enhances and/or facilitates the initiation of one or more properties (e.g.,

1 oxygen scavenging) in another compound, thus resulting in a shorter
2 induction period and/or an increase in the rate of oxygen uptake of the overall
3 system;

4

5 "induction period" means the length of time beginning with the initiation of the
6 active components of a composition and ending with the onset of one or more
7 useful properties (e.g., oxygen scavenging); and

8

9 "antioxidant" means a material which can inhibit oxidative degradation and/or
10 crosslinking of a poly polymer so as to, for example, prolong the useful
11 lifetime of the polymer, to stabilize a polymer-containing composition during
12 processing (e.g., extrusion, coating, lamination, etc.); and/or to prolong the
13 shelf-life of the composition (prior to exposure thereof to actinic or e-beam
14 radiation).

15

16 The present invention is directed to oxygen scavengers. The invention
17 includes oxygen scavenging substances, as well as compositions containing
18 same. The form of the oxygen scavengers may vary and may comprise small
19 molecules through to large macromolecules as well as those sized in
20 between. The oxygen scavengers will be characterized in that they will be
21 able to react with oxygen in their near vicinity, enabling the removal of oxygen
22 from a closed system.

23

24 While the actual form of the oxygen scavengers may vary, a characteristic
25 that they each share is they include cyclic alkene groups or functionalities,
26 which are able to react with oxygen to provide the desired oxygen scavenging
27 properties. In preferred embodiments of the present invention, this will
28 comprise a cyclohexene group i.e. a six-membered ring with double bond
29 between two adjacent carbon atoms. It is acceptable that some carbons of

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1 the cyclohexene group may also form a part of other ring structures within the
2 molecule, and/or form part of the skeleton of the molecule. It is not necessary
3 that the entire C₆ ring be dangling free of the remainder of the molecule to
4 which it is attached. A consideration however is that the group should be so
5 positioned and incorporated into the structure that the double bond is
6 available for reaction with oxygen.

7
8 It has been mentioned above that various scavengers of the present invention
9 may take different forms. This will also have some bearing on how they are
10 used, and also produced. Perhaps the simplest embodiments of the present
11 invention are short molecules containing a reactive cyclohexene group, which
12 may be dispersed in an appropriate medium for use. This may include the
13 use of short molecules (see also later) which can be dispersed within a
14 plastics resin or material. The ultimate result would be a plastics film or
15 material incorporating the oxygen scavenger. Of course, consideration would
16 need to be given to accessibility of the scavengers of the oxygen being
17 scavenged though this may rely on the porosity of the film (or film
18 layer/material) in which it is incorporated, or alternatively may be presented in
19 the manner of a coating with a reactive surface.

20
21 While the use of oxygen scavengers of varying sizes, (though typically those
22 of smaller size), dispersed through plastics materials is envisaged, oxygen
23 scavengers according to the present invention may also be used in other
24 ways.

25
26 For instance, they may be dispersed throughout non-plastics materials. This
27 may include inert and inorganic materials. This may also include other
28 liquids. It is envisaged that such embodiments of the present invention may
29 be used in applications such as sachets inserted into closed packages. The

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1 use of oxygen scavengers in sachets and package inserts is documented in
2 the art and the same principles may be applied here.

3

4 Another means by which the present invention may be applied is through the
5 use of plastics resins incorporating the desired scavenging functionalities.

6 These resins, which for instance may include polyester resins, may be used
7 in the various manners by which resins are normally used. This may include
8 film production, resin coatings, as well as molding or extrusion techniques.

9 Another method by which the present invention may be implemented is the
10 formation or modification of polymers to contain the desired scavenging
11 functionalities and groups. In such cases, the film or plastics material itself
12 will possess oxygen scavenging properties. It is envisaged that such
13 materials may exist as layers in multi-layer films. Such polymers may also be
14 introduced as copolymers or blends in film and plastics manufacturing
15 methods.

16

17 The above instances of how embodiments of the present invention may be
18 used are illustrative only. It is noted that the use of oxygen scavenging
19 materials is known in the art, and that art may be drawn upon to further
20 expand the illustrative examples given within this specification.

21

22 Embodiments of the present invention based on cyclohexene groups appear
23 to afford significant advantage over the prior art. This advantage is in the
24 number and nature of the oxidation product once the scavenging is
25 completed. In the prior art, heavily reliance is made on straight chain
26 alkenes, such as for instance fatty acids. The problem however, is that film
27 containing unsaturated compounds such as squalene or vegetable oils
28 produce large amounts of volatile aldehydes and ketones upon oxidation.
29 These tend to be released, or leach, from the plastics material over time,

1 usually find their way into the head space of the packaged material. The
2 presence of these foreign substances can represent a significant problem,
3 which the use of cyclohexene scavenging groups addresses at least partially.
4

5 In comparison, there are significantly less scission products from oxidation
6 reactions involving cyclohexene groups—the oxidation of the cyclohexene
7 group does not normally involve ring breakage. If the remainder of the
8 molecule to which the cyclohexene group is attached is bound or linked to the
9 polymeric structure of the material in which it is incorporated or affixed, or
10 otherwise bound or held in place to the material through which it is dispersed
11 or incorporated, then there is little chance of there being any free scission
12 products able to find their way from the film or material structure.
13

14 Other aspects of the present invention to some extent parallel the prior art.
15 For instance, it is desirable that the oxygen scavenging materials are
16 relatively stable (with respect to scavenging) until required. In many cases,
17 catalysis and/or triggering of any reaction is required. Photo-initiators such as
18 benzophenone may be included. Initiating or triggering by electromagnetic
19 irradiation (often in the visible through UV regions) is convenient form of
20 triggering and already used in some types of film manufacture. It is also used
21 for triggering many prior art oxygen scavengers and thus employing these
22 features and techniques of the prior art with the present invention is
23 envisaged.
24

25 As for most other oxygen scavengers relying on alkenes, some form of
26 catalyst is also required for the oxygen scavenging reactions to proceed
27 effectively. Typically transition metal catalysts are used, including their salts,
28 complexes, and other compounds. These are well documented in the prior
29 art and may also be used with the present invention as appropriate.
30

1

2

3 According to another aspect of the present invention, there is provided an
4 oxygen scavenging polymer, substantially as described above, in which the
5 reactive extrusion process comprises a transesterification process.

6

7

8

9 According to one aspect of the present invention, there is provided an oxygen
10 scavenging composition for use in or with plastics materials, said scavenger
11 comprising or including at least one cyclohexene functionality as described
12 above.

13

14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, as described above, which produces only
16 low levels of volatile or extractable (from a plastics material in which it is
17 incorporated) products as a consequence of oxygen scavenging.

18

19 According to another aspect of the present invention, there is provided an
20 oxygen scavenging composition, substantially as described herein which is
21 substantially stable with respect to reaction with oxygen until triggered by an
22 external event.

23

24 According to another aspect of the present invention, there is provided an
25 oxygen scavenging composition, substantially as described above, wherein
26 the external event is irradiation by actinic radiation or electron beam radiation.

27

28 According to a further aspect of the present invention, there is provided an
29 oxygen scavenging composition including an oxygen scavenger, substantially

1 as described above, which includes one or more trigger enhancing
2 components making the scavenger susceptible to triggering from an external
3 event.

4
5 According to another aspect of the present invention, there is provided an
6 oxygen scavenging composition, substantially as described above, wherein a
7 trigger enhancing component is a photo initiator such as benzophenone or
8 substituted derivatives thereof.

9
10 According to another aspect of the present invention, there is provided an
11 oxygen scavenging composition, substantially as described above, which
12 includes the presence of one or more catalysts for the scavenging process.

13
14 According to another aspect of the present invention, there is provided an
15 oxygen scavenging composition, substantially as described above, in which
16 the catalyst is a transition metal salt, compound or complex.

17
18 According to another aspect of the present invention, there is provided an
19 oxygen scavenging composition, substantially as described above, which is in
20 the form of a plastic resin.

21
22 According to another aspect of the present invention, there is provided an
23 oxygen scavenging composition, substantially as described above, in which
24 the plastic resin is a suitable for use in the manufacture of plastics films.

25
26 According to another aspect of the present invention, there is provided an
27 oxygen scavenging composition, substantially as described above, in which
28 the plastic resin is a polyester resin.

29

1 According to another aspect of the present invention, there is provided an
2 oxygen scavenging article comprising the oxygen scavenging composition
3 described above, where the scavenging component is present as a plastic
4 film or layer thereof.

5

6 According to another aspect of the present invention, there is provided an
7 oxygen scavenger or oxygen scavenging composition, substantially as
8 described above, when used as a polymeric material of a plastic film a layer
9 thereof, and/or a coating thereof, or in a plastic material.

10

11 According to another aspect of the present invention, there is provided an
12 oxygen scavenger or oxygen scavenging composition, substantially as
13 described above, when dispersed through a plastics film, a layer thereof,
14 and/or a coating thereon, or in a plastics material.

15

16 According to a further aspect of the present invention, there is provided an
17 oxygen scavenger or oxygen scavenging composition prepared from the
18 reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at
19 least one of a diol, a hydroxy compound or polyhydroxy compound, in the
20 presence of or absence of an esterification catalyst.

21

22 According to a further aspect of the present invention, there is provided an
23 oxygen scavenger or oxygen scavenging composition prepared from the
24 reaction of a tetrahydrophthalic anhydride or tetrahydrophthalic acid with at
25 least one of a diol, a hydroxy compound or polyhydroxy compound, in the
26 presence of or absence of an esterification catalyst.

27

28 According to a further aspect of the present invention there is provided an
29 oxygen scavenger or oxygen scavenging composition prepared from an ester

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1 or diester of a tetrahydrophthalic anhydride, in the presence of or absence of
2 a transesterification or esterification catalyst.

3

4 According to a further aspect of the present invention, there is provided an
5 oxygen scavenger or oxygen scavenging composition substantially as
6 described above, in which the anhydride comprises 1,2,3,6 tetrahydrophthalic
7 anhydride or tetrahydrophthalic anhydride monomers derived from butadiene,
8 2,3-Dimethyl-1,3-butadiene or isoprene.

9

10 According to a further aspect of the present invention, there is provided an
11 oxygen scavenging polymer including at least one cyclohexene group
12 prepared by a reactive extrusion process.

13

14 According to the present invention, a composition is provided comprising a
15 polymeric backbone, cyclic olefinic pendent groups and linking groups linking
16 the olefinic pendent groups to the polymeric backbone.

17 Also according to the present invention, an oxygen scavenging composition is
18 provided comprising a polymeric backbone, cyclic olefinic pendent groups,
19 linking groups linking the olefinic pendent groups to the polymeric backbone
20 and a transition metal catalyst.

21 Also according to the present invention, an article of manufacture is provided
22 which is suitable as a container, the container inhibiting oxidation of contents
23 of the container by removing oxygen from the container and by inhibiting
24 ingress of oxygen into the container from outside the container, the article
25 comprising an oxygen scavenging composition which comprises a polymeric
26 backbone, cyclic olefinic pendent groups, linking groups linking the olefinic
27 pendent groups to the backbone, and a transition metal catalyst.

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1 Also according to the present invention, a layer suitable for scavenging
 2 oxygen is provided which comprises (a) a polymer backbone; (b) cyclic
 3 olefinic pendent groups; (c) linking groups linking the backbone with the
 4 pendent groups; and (d) a transition metal catalyst.

5 Also according to the present invention, a process of making a polymer
 6 material is provided, the process being selected from the group consisting of
 7 esterification, transesterification, amidation, transamidation and direct
 8 polymerization, in which the oxygen scavenging packaging material
 9 comprises a polymer backbone, cyclic olefinic pendent groups, linking groups
 10 linking the backbone with the pendent groups.

11 In a preferred embodiment of the invention, the polymeric backbone of the
 12 above compositions, article, layer and process is ethylenic and the linking
 13 groups are selected from the group consisting of:

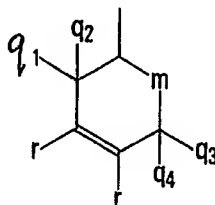
14 $-\text{O}-(\text{CHR})_n-; -(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-; -\text{NH}-(\text{CHR})_n-; -\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-;$

15 $-(\text{C}=\text{O})-\text{NH}-(-\text{CHR})_n-;$ and $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-;$

16 wherein R is hydrogen or an alkyl group selected from the group consisting of
 17 methyl, ethyl, propyl and butyl groups and where n is an integer in the range
 18 from 1 to 12.

19 In a more preferred embodiment of the invention, the cyclic olefinic pendent
 20 groups of the above compositions, article, layer and process have the
 21 structure (II):

(II)



1

2 where q_1 , q_2 , q_3 , q_4 , and r are selected from the group consisting of $-H$, $-CH_3$,
3 and $-C_2H_5$; and where m is $-(CH_2)_n-$ with n being an integer in the range from 0
4 to 4; and wherein, when r is $-H$, at least one of q_1 , q_2 , q_3 and q_4 is $-H$.

5 In another preferred embodiment of the invention, the polymeric backbone of
6 the above compositions, article, layer and process comprises monomers
7 selected from the group consisting of ethylene and styrene.

8 In yet another preferred embodiment of invention, the cyclic olefinic pendent
9 groups of the above compositions, article, layer and process are grafted onto
10 the linking groups of the polymeric backbone by a esterification,
11 transesterification, amidation or transamidation reaction.

12 In still another preferred embodiment of the invention, the esterification,
13 transesterification, amidation or transamidation reaction of the above
14 compositions, article, layer and process is a solution reaction or a reactive
15 extrusion.

16 In another preferred embodiment of the invention, the esterification,
17 transesterification, amidation or transamidation reaction of the above
18 compositions, article, layer and process is catalyzed by a catalyst selected
19 from the group consisting of strong non-oxidizing acids, tertiary amines,
20 Group I alkoxides, Group IVB alkoxides, and Group IVA organometallics.

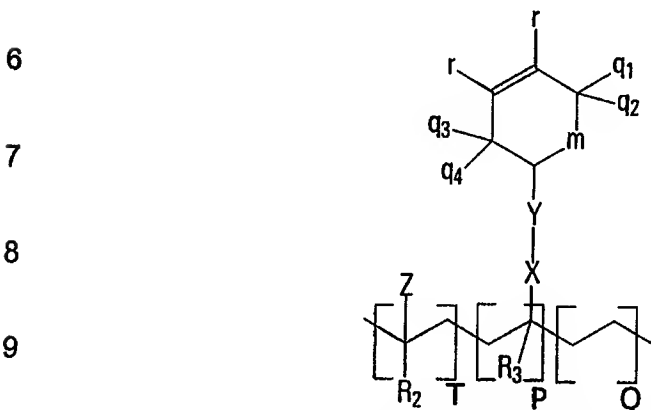
21 In yet another preferred embodiment of invention, the catalyst of the above
22 compositions, article, layer and process is selected from a group consisting of
23 toluene sulfonic acid, sodium methoxide, tetrabutyl titanate, tetraisopropyl
24 titanate, tetra-*n*-propyl-titanate, tetraethyl titanate, 2-hydroxy-pyridine and
25 dibutyltin dilaurate.

26

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1 In still another preferred embodiment of the invention, the polymeric
 2 backbone, linking groups and cyclic olefin pendent groups of the above
 3 compositions, article, layer and process comprise repeating units, each unit
 4 having a structure (III) as follows:

5 (III)

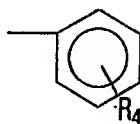


10 wherein $P+T+Q$ is 100 mol % of the total composition; P is greater than 0
 11 mol % of the tot

12 al composition; Z is selected from the group consisting of an aryl group;
 13 $-(C=O)OR_1$; $-O(C=O)R_1$; and an alkyl aryl group, structure (IV):

14 (IV)

15



16 where R_4 is selected from the group consisting of $-CH_3$, $-C_2H_5$, and $-H$; R_1 is
 17 selected from the group consisting of $-H$, $-CH_3$, $-C_2H_5$, $-C_3H_7$ and $-C_4H_9$; R_2 and
 18 R_3 are selected from the group consisting of $-H$ and $-CH_3$; X is selected from
 19 the group consisting of $-O-$, $-NH-$, $-(C=O)O-$, $-(C=O)NH-$, $-(C=O)S-$, $-O(C=O)-$
 20 and $-(CHR)_\ell$; ℓ is an integer in the range from 1 to 6; Y is $-(CHR)_n$, where n is
 21 an integer in the range from 0 to 12, R being selected from the group
 22 consisting of $-H$, $-CH_3$ and $-C_2H_5$; where q_1 , q_2 , q_3 , q_4 , and r are selected from
 23 the group consisting of $-H$, $-CH_3$, and $-C_2H_5$; and where m is $-(CH_2)_n$ and

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1 where n is an integer in the range from 0 to 4; and wherein when r is -H, at
2 least one of q_1 , q_2 , q_3 and q_4 is -H.

3 In another preferred embodiment of the invention, the cyclic olefinic pendent
4 groups of the above compositions, article, layer and process are selected
5 from the group consisting of cyclohexene-4-methylene radical, 1-methyl
6 cyclohexene-4-methylene radical, 2-methyl cyclohexene-4-methylene radical,
7 5-methyl cyclohexene-4-methylene radical, 1,2-dimethyl cyclohexene-4-
8 methylene radical, 1,5-dimethyl cyclohexene-4-methylene radical,
9 2,5-dimethyl cyclohexene-4-methylene radical, 1,2,5-trimethyl cyclohexene-4-
10 methylene radical, cyclohexene-4-ethylene radical, 1-methyl cyclohexene-4-
11 ethylene radical, 2-methyl cyclohexene-4-ethylene radical, 5-methyl
12 cyclohexene-4-ethylene radical, 1,2-dimethyl cyclohexene-4-ethylene radical,
13 1,5-dimethyl cyclohexene-4-ethylene radical, 2,5-dimethyl cyclohexene-4-
14 ethylene radical, 1,2,5-trimethyl cyclohexene-4-ethylene radical, cyclohexene-
15 4-propylene radical, 1-methyl cyclohexene-4-propylene radical, 2-methyl
16 cyclohexene-4-propylene radical, 5-methyl cyclohexene-4-propylene radical,
17 1,2-dimethyl cyclohexene-4-propylene radical, 1,5-dimethyl cyclohexene-4-
18 propylene radical, 2,5-dimethyl cyclohexene-4-propylene radical,
19 1,2,5-trimethyl cyclohexene-4-propylene radical, cyclopentene-4-methylene
20 radical, 1-methyl cyclopentene-4-methylene radical, 3-methyl cyclopentene-4-
21 methylene radical, 1,2-dimethyl cyclopentene-4-methylene radical,
22 3,5-dimethyl cyclopentene-4-methylene radical, 1,3-dimethyl cyclopentene-4-
23 methylene radical, 2,3-dimethyl cyclopentene-4-methylene radical,
24 1,2,3-trimethyl cyclopentene-4-methylene radical, 1,2,3,5-tetramethyl
25 cyclopentene-4-methylene radical, cyclopentene-4-ethylene radical, 1-methyl
26 cyclopentene-4-ethylene radical, 3-methyl cyclopentene-4-ethylene radical,
27 1,2-dimethyl cyclopentene-4-ethylene radical, 3,5-dimethyl cyclopentene-4-
28 ethylene radical, 1,3-dimethyl cyclopentene-4-ethylene radical, 2,3-dimethyl
29 cyclopentene-4-ethylene radical, 1,2,3-trimethyl cyclopentene-4-ethylene

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1 radical, 1,2,3,5-tetramethyl cyclopentene-4-ethylene radical, cyclopentene-4-
2 propylene radical, 1-methyl cyclopentene-4-propylene radical, 3-methyl
3 cyclopentene-4-propylene radical, 1,2-dimethyl cyclopentene-4-propylene
4 radical, 3,5-dimethyl cyclopentene-4-propylene radical, 1,3-dimethyl
5 cyclopentene-4-propylene radical, 2,3-dimethyl cyclopentene-4-propylene
6 radical, 1,2,3-trimethyl cyclopentene-4-propylene radical, and
7 1,2,3,5-tetramethyl cyclopentene-4-propylene radical.

8 In yet another preferred embodiment of the invention, the composition of the
9 above compositions, article, layer and process is a ethylene/methyl
10 acrylate/cyclohexenyl methyl acrylate terpolymer, a cyclohexenyl methyl
11 acrylate/ethylene copolymer, a cyclohexenyl methyl methacrylate/styrene
12 copolymer, a cyclohexenyl methyl acrylate homopolymer or a methyl
13 acrylate/cyclohexenyl methyl acrylate copolymer.

14

15 In another preferred embodiment of the invention, the odor and taste
16 characteristics of products packaged with material comprised of the above
17 compositions, article, layer and process are not adulterated as a result of
18 oxidation of the composition.

19

20 In still another preferred embodiment of the invention, there is no significant
21 fragmentation of the olefinic pendent groups and linking groups from the
22 polymeric backbone as a result of oxidation of the above compositions,
23 article, layer and process.

24

25 In yet another preferred embodiment of the invention, the transition metal
26 catalyst of the above oxygen scavenging composition, article of manufacture,
27 layer and process is a metal salt.

28

1 In still another preferred embodiment of the invention, the metal in the metal
2 salt of the above oxygen scavenging composition, article of manufacture,
3 layer and process is cobalt.

4 In still another preferred embodiment of the invention, the metal salt of the
5 above oxygen scavenging composition, article of manufacture, layer and
6 process is selected from the group consisting of cobalt neodecanoate, cobalt
7 2-ethylhexanoate, cobalt oleate and cobalt stearate.

8

9 In yet another preferred embodiment of the invention, the composition of the
10 above oxygen scavenging composition, article of manufacture, layer and
11 process further comprises at least one triggering material to enhance initiation
12 of oxygen scavenging.

13

14 In still another preferred embodiment of the invention, the triggering material
15 of the above oxygen scavenging composition, article of manufacture, layer
16 and process is a photo initiator.

17

18 In a preferred embodiment of the invention, the above article of manufacture
19 is a package.

20

21 In another preferred embodiment of invention, the package article of the
22 above article of manufacture comprises a flexible film having a thickness of at
23 most 10 mil or a flexible sheet having a thickness of at least 10 mil.

24

25 In yet another preferred embodiment of the invention, the oxygen scavenging
26 system of the package article of the above article of manufacture comprises
27 at least one additional layer selected from among oxygen barrier layers,
28 polymeric selective layers, and heat seal layers.

29

1 In still another preferred embodiment of the invention, the above article of
2 manufacture is a package with a food product located within the package.

3 In yet another preferred embodiment of the invention, the above article of
4 manufacture is a package for packaging a cosmetic, chemical, electronic
5 device, pesticide or a pharmaceutical composition.

6

7 In still another preferred embodiment of the invention, a multi-layer film
8 comprises the article of the above article of manufacture and the film has at
9 least one additional functional layer.

10

11 In yet another preferred embodiment of the invention, the multi-layer film of
12 the above article of manufacture has at least one additional layer selected
13 from among oxygen barrier layers, polymeric selective barrier layers,
14 structural layers and heat seal layers.

15

16 In still another preferred embodiment of the invention, the multi-layer film of
17 the above article of manufacture has at least one additional layer which is an
18 oxygen barrier layer.

19

20 In yet another preferred embodiment of the invention, the multi-layer film of
21 the above article of manufacture further comprises at least one polymeric
22 selective barrier layer.

23

24 In still another preferred embodiment of the invention, the multi-layer film of
25 the above article of manufacture further comprises at least one heat seal
26 layer.

27

28 In yet another preferred embodiment of the invention, the multi-layer film of
29 the above article of manufacture further comprises at least one structural
30 layer.

1 In still another preferred embodiment of the invention, the above article of
2 manufacture is a rigid container, sealing gasket, patch, container closure
3 device, bottle cap, bottle cap insert or molded or thermoformed shape.

4
5 In yet another preferred embodiment of the invention, the molded or
6 thermoformed shape of the above article of manufacture is a bottle or tray.

7
8 In still another preferred embodiment of the invention, the above layer in
9 addition comprises polymeric diluent.

10
11 In yet another preferred embodiment of the invention, the diluent of the above
12 layer is a thermoplastic polymer.

13
14 In still another preferred embodiment of the invention, the above layer is
15 adjacent to one or more additional layers.

16
17 In still another preferred embodiment of the invention, at least one of the
18 additional layers adjacent to the above layer is an oxygen barrier.

19
20 In still another preferred embodiment of the invention, the oxygen barrier of
21 the above layer comprises a member of the group consisting of poly(ethylene-
22 vinyl alcohol), polyacrylonitrile, poly(vinyl chloride), polyamides,
23 poly(vinylidene dichloride), poly(ethylene terephthalate), silica, metal foil and
24 metalized polymeric films.

25
26 In still another preferred embodiment of the invention, the one or more of said
27 additional layer or layers of the above layer is coextruded with the above
28 layer.

29

1 In yet another preferred embodiment of the invention, the one or more of said
2 additional layer or layers of the above layer is laminated onto the above layer.

3

4 In still another preferred embodiment of the invention, the one or more of said
5 additional layer or layers of the above layer is coated onto the above layer.

6

7 In yet another preferred embodiment of the invention, the above layer is
8 flexible.

9

10 In still another preferred embodiment of the invention, the above layer is
11 transparent.

12

13 In yet another preferred embodiment of the invention, an article for packaging
14 wherein the article comprises the above layer.

15

16 In yet another preferred embodiment of the invention, the above process of
17 making the oxygen scavenging packaging material comprises the steps of:

18 (a) selecting polymers from the group consisting of styrene/maleic
19 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
20 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
21 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
22 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
23 and styrene/methyl methacrylate to form a mixture and combining the
24 polymers with an esterifying/transesterifying compound selected from
25 the group consisting of cyclohexene-4-methanol, 1-methyl cyclohexene-
26 4-methanol, 2-methyl cyclohexene-4-methanol, 5-methyl cyclohexene-4-
27 methanol, 1,2-dimethyl cyclohexene-4-methanol, 1,5-dimethyl
28 cyclohexene-4-methanol, 2,5-dimethyl cyclohexene-4-methanol,

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- 1 1,2,5-trimethyl cyclohexene-4-methanol, cyclohexene-4-ethanol,
2 1-methyl cyclohexene-4-ethanol, 2-methyl cyclohexene-4-ethanol,
3 5-methyl cyclohexene-4-ethanol, 1,2-dimethyl cyclohexene-4-ethanol,
4 1,5-dimethyl cyclohexene-4-ethanol, 2,5-dimethyl cyclohexene-4-
5 ethanol, 1,2,5-trimethyl cyclohexene-4-ethanol, cyclohexene-4-propanol,
6 1-methyl cyclohexene-4-propanol, 2-methyl cyclohexene-4-propanol,
7 5-methyl cyclohexene-4-propanol, 1,2-dimethyl cyclohexene-4-propanol,
8 1,5-dimethyl cyclohexene-4-propanol, 2,5-dimethyl cyclohexene-4-
9 propanol, 1,2,5-trimethyl cyclohexene-4-propanol, cyclopentene-4-
10 methanol, 1-methyl cyclopentene-4-methanol, 3-methyl cyclopentene-4-
11 methanol, 1,2-dimethyl cyclopentene-4-methanol, 3,5-dimethyl
12 cyclopentene-4-methanol, 1,3-dimethyl cyclopentene-4-methanol,
13 2,3-dimethyl cyclopentene-4-methanol, 1,2,3-trimethyl cyclopentene-4-
14 methanol, 1,2,3,5-tetramethyl cyclopentene-4-methanol, cyclopentene-
15 4-ethanol, 1-methyl cyclopentene-4-ethanol, 3-methyl cyclopentene-4-
16 ethanol, 1,2-dimethyl cyclopentene-4-ethanol, 3,5-dimethyl
17 cyclopentene-4-ethanol, 1,3-dimethyl cyclopentene-4-ethanol,
18 2,3-dimethyl cyclopentene-4-ethanol, 1,2,3-trimethyl cyclopentene-4-
19 ethanol, 1,2,3,5-tetramethyl cyclopentene-4-ethanol, cyclopentene-4-
20 propanol, 1-methyl cyclopentene-4-propanol, 3-methyl cyclopentene-4-
21 propanol, 1,2-dimethyl cyclopentene-4-propanol, 3,5-dimethyl
22 cyclopentene-4-propanol, 1,3-dimethyl cyclopentene-4-propanol,
23 2,3-dimethyl cyclopentene-4-propanol, 1,2,3-trimethyl cyclopentene-4-
24 propanol, and 1,2,3,5-tetramethyl cyclopentene-4-propanol;
- 25 (b) heating the polymers and esterifying/transesterifying compounds
26 selected in (a) to form a polymer melt;
- 27 (c) processing the melt in an extruder under esterification/transesterification
28 conditions with esterification/transesterification catalysts and

1 antioxidants protecting the melt from oxidation during extrusion, so that
2 the polymer melt undergoes esterification of polymeric anhydrides with
3 cyclic olefin pendent groups, esterification of polymeric acids with cyclic
4 olefin pendent groups or exchange of alkyl groups of polymeric esters
5 with cyclic olefin pendent groups; and

6 (d) removing volatile organic products and by-products from the melt.

7 In still another preferred embodiment of the invention, the above process of
8 making the oxygen scavenging packaging material comprises the steps of:

9 (a) selecting polymers from the group consisting of styrene/maleic
10 anhydride, ethylene/maleic anhydride, ethylene/acrylic acid,
11 ethylene/methacrylic acid, acrylic acid, methacrylic acid,
12 styrene/methacrylic acid, ethylene/methyl acrylate, ethylene/ethyl
13 acrylate, ethylene/butyl acrylate, methyl methacrylate, methyl acrylate,
14 and styrene/methyl methacrylate to form a mixture and combining the
15 polymers with an amidizing/transamidizing compound selected from the
16 group consisting of cyclohexene-4-methyl amine, 1-methyl cyclohexene-
17 4-methyl amine, 2-methyl cyclohexene-4-methyl amine, 5-methyl
18 cyclohexene-4-methyl amine, 1,2-dimethyl cyclohexene-4-methyl amine,
19 1,5-dimethyl cyclohexene-4-methyl amine, 2,5-dimethyl cyclohexene-4-
20 methyl amine, 1,2,5-trimethyl cyclohexene-4-methyl amine,
21 cyclohexene-4-ethyl amine, 1-methyl cyclohexene-4-ethyl amine,
22 2-methyl cyclohexene-4-ethyl amine, 5-methyl cyclohexene-4-ethyl
23 amine, 1,2-dimethyl cyclohexene-4-ethyl amine, 1,5-dimethyl
24 cyclohexene-4-ethyl amine, 2,5-dimethyl cyclohexene-4-ethyl amine,
25 1,2,5-trimethyl cyclohexene-4-ethyl amine, cyclohexene-4-propyl amine,
26 1-methyl cyclohexene-4-propyl amine, 2-methyl cyclohexene-4-propyl
27 amine, 5-methyl cyclohexene-4-propyl amine, 1,2-dimethyl cyclohexene-
28 4-propyl amine, 1,5-dimethyl cyclohexene-4-propyl amine, 2,5-dimethyl

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- 1 cyclohexene-4-propyl amine, 1,2,5-trimethyl cyclohexene-4-propyl
2 amine, cyclopentene-4-methyl amine, 1-methyl cyclopentene-4-methyl
3 amine, 3-methyl cyclopentene-4-methyl amine, 1,2-dimethyl
4 cyclopentene-4-methyl amine, 3,5-dimethyl cyclopentene-4-methyl
5 amine, 1,3-dimethyl cyclopentene-4-methyl amine, 2,3-dimethyl
6 cyclopentene-4-methyl amine, 1,2,3-trimethyl cyclopentene-4-methyl
7 amine, 1,2,3,5-tetramethyl cyclopentene-4-methyl amine, cyclopentene-
8 4-ethyl amine, 1-methyl cyclopentene-4-ethyl amine, 3-methyl
9 cyclopentene-4-ethyl amine, 1,2-dimethyl cyclopentene-4-ethyl amine,
10 3,5-dimethyl cyclopentene-4-ethyl amine, 1,3-dimethyl cyclopentene-4-
11 ethyl amine, 2,3-dimethyl cyclopentene-4-ethyl amine, 1,2,3-trimethyl
12 cyclopentene-4-ethyl amine, 1,2,3,5-tetramethyl cyclopentene-4-ethyl
13 amine, cyclopentene-4-propyl amine, 1-methyl cyclopentene-4-propyl
14 amine, 3-methyl cyclopentene-4-propyl amine, 1,2-dimethyl
15 cyclopentene-4-propyl amine, 3,5-dimethyl cyclopentene-4-propyl
16 amine, 1,3-dimethyl cyclopentene-4-propyl amine, 2,3-dimethyl
17 cyclopentene-4-propyl amine, 1,2,3-trimethyl cyclopentene-4-propyl
18 amine, and 1,2,3,5-tetramethyl cyclopentene-4-propyl amine;
- 19 (b) heating the polymers and amidizing/transamidizing compounds selected
20 in (a) to form a polymer melt;
- 21 (c) processing the melt in an extruder under amidation/transamidation
22 conditions with amidation/transamidation catalysts and antioxidants
23 protecting the melt from oxidation during extrusion, so that the polymer
24 melt undergoes amidation of polymeric anhydrides with cyclic olefin
25 pendent groups, amidation of polymeric acids with cyclic olefin pendent
26 groups or exchange of alkyl groups of polymeric esters with cyclic olefin
27 pendent groups; and
- 28 (d) removing volatile organic products and by-products from the melt.

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1 In yet another preferred embodiment of the invention, the above process of
2 making of the oxygen scavenging packaging material comprises the steps of:
3 (a) adding to an autoclave, ethylene and a vinyl monomer comprising a
4 pendent cyclohexene;
5
6 (b) stirring the ethylene and the vinyl monomer in the autoclave to achieve a
7 mixture;
8
9 (c) adding a polymerization initiator before, during or after the stirring step;
10
11 (d) polymerizing the mixture to achieve a polymer; and
12
13 (e) isolating and purifying the polymer.
14

15 In still another embodiment of the invention, in the above process, in step (a),
16 an alpha-olefin is added to the autoclave along with the ethylene and the vinyl
17 monomer and, in step (b), the alpha-olefin is stirred with the ethylene and the
18 vinyl monomer to achieve the mixture.
19

20 The present invention relates to a non-odorous oxygen scavenging polymer
21 composition comprising: (1) monomers derived from cyclic hydrocarbon
22 moieties having at least one cyclic allylic or cyclic benzylic hydrogen and (2) a
23 transition metal oxidation catalyst. The present invention also relates to a
24 rigid container for food or beverage, the container being molded from a resin
25 comprising the above-described non-odorous oxygen scavenging polymer
26 composition. The present invention also relates to the above-described rigid
27 container further comprising a tinted ultraviolet protection layer, which may or
28 may not be the food contact layer, located between the layer comprising the
29 non-odorous oxygen scavenging composition and the inside of the rigid
30 container.

1 In a preferred embodiment of the above non-odorous oxygen scavenging
2 polymer composition, wherein the composition comprises a vinyl polymer
3 selected from the group consisting of ethylene polymer, ethylene copolymer,
4 propylene polymer, propylene copolymer, styrene polymer, styrene copolymer
5 and mixtures thereof.

6

7 In another preferred embodiment of the above non-odorous oxygen
8 scavenging polymer composition, the composition comprises condensation
9 polymers selected from the group consisting of polyesters, polyamides,
10 polycarbonate, polyurethane, polyureas and polyether.

11

12 In a more preferred embodiment of the above composition comprising
13 condensation polymers, the composition is thermoplastic.

14

15 In another more preferred embodiment of the above composition comprising
16 condensation polymers, the composition is thermoset.

17

18 In yet another more preferred embodiment of the above composition
19 comprising condensation polymers, the composition is a multilayered
20 structure with other layers being an aromatic polyester or copolyester
21 selected from the group consisting of polyethylene terephthalate,
22 polyethylene naphthalate, polypropylene terephthalate, polybutylene
23 terephthalate, polyethylene isophthalate, polycyclohexanedimethanol
24 terephthalate, polybutylene naphthalate, polycyclohexanedimethanol
25 naphthalate, and copolymers and blends thereof.

26

27 In still another more preferred embodiment of the above composition
28 comprising condensation polymers, the composition is a multilayered
29 structure with other layers being polyamides or copolyamides selected from
30 the group consisting of Nylon 6, Nylon 66, Nylon 610 and mixtures thereof.

1 In yet another more preferred embodiment of the above composition
2 comprising condensation polymers, the composition is a multilayered
3 structure with other layers being bisphenol A carbonate.

4

5 In yet another more preferred embodiment of the above composition
6 comprising condensation polymers, the composition is a multilayered
7 structure with other layers being vinylic polymers or copolymers selected
8 from the group consisting of ethylene polymer, ethylene copolymer, propylene
9 polymer, propylene copolymer, styrene polymer, styrene copolymer, acrylate
10 polymer, acrylate copolymer, vinyl chloride polymer, vinyl chloride copolymer,
11 divinyl chloride polymer, divinyl chloride copolymer, fluorinated vinyl polymer,
12 fluorinated vinyl copolymer and mixtures thereof.

13

14 In still another more preferred embodiment of the above composition
15 comprising condensation polymers, the composition is blended with an
16 aromatic polyester or copolyester selected from the group consisting of
17 polyethylene terephthalate, polyethylene naphthalate, polypropylene
18 terephthalate, polybutylene terephthalate, polyethylene isophthalate,
19 polycyclohexanedimethanol terephthalate, polybutylene naphthalate,
20 polycyclohexanedimethanol naphthalate, and copolymers and blends thereof.

21

22 In yet another more preferred embodiment of the above composition
23 comprising condensation polymers, the composition is blended with
24 polyamides or copolyamides selected from the group consisting of Nylon 6,
25 Nylon 66, Nylon 610 and mixtures thereof.

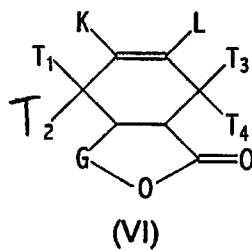
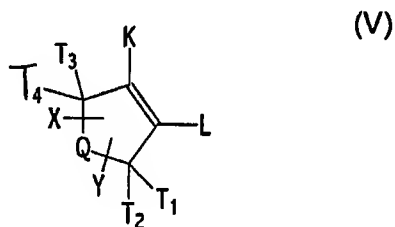
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27 In still another more preferred embodiment of the above composition
28 comprising condensation polymers, the composition is blended with bisphenol
29 A polycarbonate.

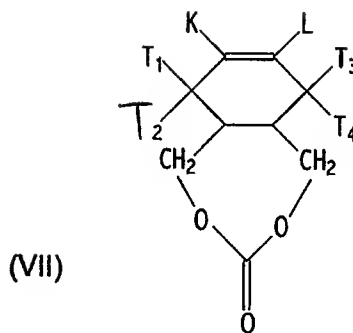
1 In yet another more preferred embodiment of the above composition
 2 comprising condensation polymers, the composition being a blend comprising
 3 vinylic polymers or copolymers selected from the group consisting of ethylene
 4 polymer, ethylene copolymer, propylene polymer, propylene copolymer,
 5 styrene polymer, styrene copolymer, acrylate polymer, acrylate copolymer,
 6 vinyl chloride polymer, vinyl chloride copolymer, divinyl chloride polymer,
 7 divinyl chloride copolymer, fluorinated vinyl polymer, fluorinated vinyl
 8 copolymer and mixtures thereof.

9
 10 In a more preferred embodiment of the above composition comprising
 11 condensation polymers, the composition is laminated or adhering onto a
 12 substrate selected from the group consisting of paper, foil, high temperature
 13 film, metallized film, polyamide films, ethylene vinyl alcohol film, silica coated
 14 film, nylon/EVOH/nylon, oriented polypropylene, polyester film, polyethylene,
 15 polypropylene, polyester, oriented polyethylene terephthalate and cellophane.

16
 17 In another preferred embodiment of the above non-odorous oxygen
 18 scavenging polymer composition, the cyclic allylic monomers are selected
 19 from the group consisting of structure (V), structure (VI) and structure (VII):

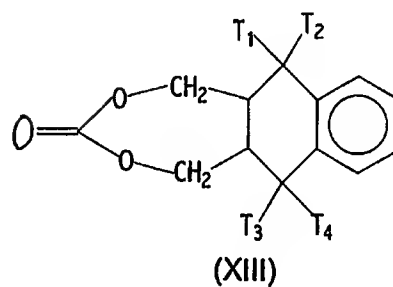
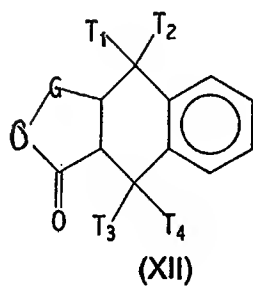
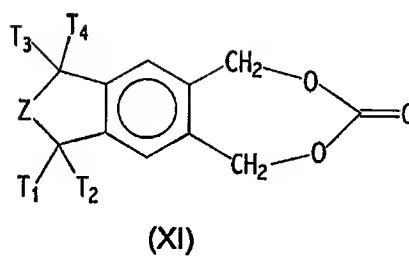
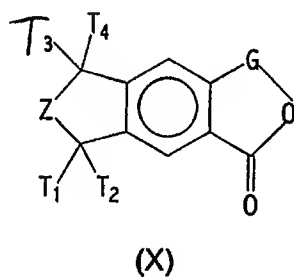
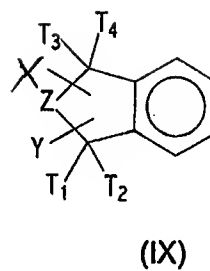
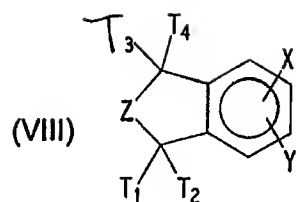


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with K, L, T₁, T₂, T₃, and T₄ being selected from the group consisting of -C_qH_{2q+1} with q being an integer in the range from 0 to 12 and wherein, when either K or L is -H, at least one of T₁, T₂, T₃ and T₄ is -H; and with X and Y being selected from the group consisting of -(CH₂)_n-OH, -(CH₂)_n-NH₂, -(CH₂)_nNC=O and -(CH₂)_m-(C=O)-A with n being an integer in the range from 1 to 12 and m being an integer in the range from 0 to 12 and A being selected from the group consisting of -OH, -OCH₃, -OC₂H₅, -OC₃H₇, and halides; and Q being selected from the group consisting of -(C_tH_{2t+2}) with t being an integer in the range from 1 to 4; and with G being selected from -(C=O)- and -(C_nH_{2n+1})- with n being an integer from 0 to 12.

In yet another more preferred embodiment of the above non-odorous oxygen scavenging polymer composition, the cyclic benzylic monomers are selected from the group consisting of structure (VIII), structure (IX), structure (X), structure (XI), structure (XII), and structure (XIII)



where X and Y are selected from the group consisting of $-(CH_2)_n-OH$,
 $-(CH_2)_n-NH_2$ and $-(CH_2)_m-(C=O)-R_1$ with n being an integer in the range

1 from 1 to 12, and with m being an integer in the range from 0 to 12 and
2 with R_1 being selected from the group consisting of $-\text{OH}$, $-\text{OCH}_3$,
3 $-\text{OC}_2\text{H}_5$, $-\text{OC}_3\text{H}_7$ and halides;
4 with T_1 , T_2 , T_3 , and T_4 being selected from the group consisting of
5 $-\text{C}_q\text{H}_{2q+1}$ with q being an integer in the range from 0 to 12 and at least
6 one of T_1 , T_2 , T_3 and T_4 being $-\text{H}$;
7 and with X and Y being selected from the group consisting of –
8 $(\text{CH}_2)_n-\text{OH}$, $-(\text{CH}_2)_n-\text{NH}_2$, $-(\text{CH}_2)_n\text{NC}=\text{O}$, and $-(\text{CH}_2)_m-(\text{C}=\text{O})-\text{A}$ with n
9 being an integer in the range from 1 to 12, and m being an integer in the
10 range from 0 to 12 and A being selected from the group consisting of
11 $-\text{OH}$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$, $-\text{OC}_3\text{H}_7$ and halides; and Z being selected from the
12 group consisting of $-(\text{C}_t\text{H}_{2t-2})-$, $-\text{O}-$, $-\text{NR}_2-$, $-\text{S}-$, with t being an integer in
13 the range from 1 to 4 and R_2 being selected from the group consisting of
14 $-\text{OH}$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$, $-\text{OC}_3\text{H}_7$ and halides;
15 and with G being selected from $-(\text{C}=\text{O})-$ and $-(\text{C}_n\text{H}_{2n+1})-$ with n being an
16 integer from 0 to 12.

17 In still another more preferred embodiment, the composition of the resin of the
18 above-described rigid container is a single layer.

19

20 In yet another more preferred embodiment, the composition of the resin of the
21 above-described rigid container is multilayered.

22

23 In yet another more preferred embodiment, the composition of the resin of the
24 above-described rigid container comprises an outer air contact layer and an
25 inner oxygen scavenging layer.

26

27 In still another more preferred embodiment, the outer air contact layer of the
28 composition of the resin of the above-described rigid container comprises an
29 oxygen barrier resin selected from the group consisting of polyethylene

1 terephthalate, polyethylene naphthalate and a mixture of polyethylene
2 terephthalate and polyethylene naphthalate.

3

4 In yet another more preferred embodiment, the composition of the resin of the
5 above-described rigid container further comprises at least one of an inner
6 food contact layer, a tie layer, and a tinted ultraviolet protection layer.

7

8 In still another more preferred embodiment, the inner food contact layer of the
9 composition of the resin of the above-described rigid container comprises an
10 oxygen barrier resin selected from the group consisting of polyethylene
11 terephthalate, polyethylene naphthalate and a mixture of polyethylene
12 terephthalate and polyethylene naphthalate.

13

14 In yet another more preferred embodiment, the oxygen scavenging of the
15 composition of the resin of the above-described rigid container is initiated by
16 moisture or actinic radiation.

17 In still another more preferred embodiment, the transition metal catalyst of the
18 composition of the resin of the above-described rigid container is a metal salt.

19

20 In yet another more preferred embodiment, the metal in the metal salt of the
21 transition metal catalyst of the composition of the resin of the above-
22 described rigid container is cobalt.

23

24 In still another more preferred embodiment, the metal salt of the transition
25 metal catalyst of the composition of the resin of the above-described rigid
26 container is selected from the group consisting of cobalt neodecanoate,
27 cobalt 2-ethylhexanoate, cobalt oleate and cobalt stearate.

28

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1 In yet another more preferred embodiment, the composition of the resin of the
2 above-described rigid container further comprises at least one triggering
3 material to enhance initiation of oxygen scavenging.

4
5 In still another more preferred embodiment, the triggering material of the resin
6 of the composition of the above-described rigid container is a photoinitiator.

7
8 In yet another more preferred embodiment, the photoinitiator of the resin of
9 the composition of the above-described rigid container has an ultraviolet
10 absorption window above 320 nm.

11
12 In still another more preferred embodiment, the above-described rigid
13 container is suitable for packaging oxygen sensitive drinks for extended
14 freshness and shelf life.

15
16 In yet another more preferred embodiment, the above-described rigid
17 container is suitable for packaging beer.

18

19 DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a schematic showing the overall process leading to the
21 transesterification of ethylene methyl acrylate copolymers (EMAC) to give
22 modified EMAC having cyclic pendent olefins.

23 Figure 2 is a graph comparatively plotting percent oxygen in headspace at
24 4°C (initially at 1% oxygen) against time in days for two 3-layer film extrusions
25 based on Dowlex® 3010/EMCM/Dowlex® 3010 films (EMCM being an
26 acronym for ethylene/methyl acrylate/cyclohexenyl methyl acrylate terpolymer
27 also referred to as poly(ethylene/methyl acrylate/cyclohexene-methyl
28 acrylate)), both including the EMCM inner layer and one of them having

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1 50 ppm of a non-volatile antioxidant Irganox® 1010 in the EMCM layer and
2 one of them having 100 ppm Irganox® 1010 in the EMCM layer.

3 Figure 3 is a graph comparatively plotting percent oxygen in headspace at
4 4°C (initially at 1% oxygen) against time in days for an EMCM film and two
5 EBAC blended EMCM films, one of them having 3:1 EBAC:EMCM and one of
6 them having 1:1 EBAC:EMCM.

7 Figure 4 is a graph comparatively plotting the oxygen scavenging rates and
8 capacities at 25°C in which the initial headspace oxygen was 21% (air) for an
9 EMCM film and a 2:1 EBAC:EMCM film.

10 Figure 5 is a graph showing the taste ratings in a comparative taste test
11 between food stored in two oxygen scavenging packages (EMCM and SBS)
12 and a control package (no oxygen scavenger).

13

14

15

16

DETAILED DESCRIPTION OF THE INVENTION

17

18 We have found that materials containing certain cyclohexenyl functionalities
19 are excellent oxygen absorbers when compounded with a transition metal salt
20 and optionally a photoinitiator, and that when these materials oxidize they
21 produce very low levels of oxidation byproducts. This is in marked contrast to
22 the known art, where excellent oxygen absorbers can be obtained from the
23 use of linear unsaturated compounds compound with a transition metal salt,
24 and a photoinitiator, but where the levels of oxidation byproducts are
25 excessively high. It is thought that this improvement is obtained because mild
26 oxidation of cyclohexene does not break bonds on the ring structure whilst
27 oxidation of linear unsaturated material such as linoleic acid or vegetable oil

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1 under similar conditions produces smaller molecules by chain scission. When
2 incorporated into polymers, the cyclohexene containing systems are found to
3 produce considerably less volatile byproducts than the linear unsaturated
4 materials.

5 The compositions of this invention are significantly cleaner than those
6 described in the prior art, they do not require the use of high levels of adjuncts
7 to absorb the undesirable byproducts. Such absorbent additives are known in
8 the art, for example see U.S. 5,834,079 and U.S. 08/857,276. It is also well
9 known in the art that such additives (zeolites and silicas) adversely affect the
10 haze and clarity of packaging structures.

11

12 The oxygen scavenging compositions consist of:

13 (a) a polymer or lower molecular weight material containing substituted
14 cyclohexene functionality according to the following structure (I):

15

16

17

18

19

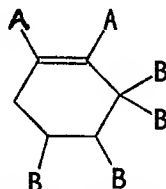
(I)

20

21

22

23



24 where A may be hydrogen or methyl and either one or two of the B groups is
25 a heteroatom containing linkage which attaches the cyclohexene ring to
26 the said material. The remaining B groups are hydrogen or methyl;

27

28 (b) a transition metal catalyst;

1

2 (c) an optional photoinitiator.

3

4 The compositions may be polymeric in nature or they may be lower molecular
5 weight materials. In either case, they may be blended with further polymers
6 or other additives. In the case of low molecular weight materials they will
7 most likely be compounded with a carrier resin before use. The following
8 examples represent some applications of various embodiments of the present
9 invention currently envisaged by the patentee. These examples are not
10 meant to be limiting nor exhaustive but merely illustrative of how the present
11 invention may be used, or applied to address problems associated with the
12 prior art.

13

14

15 The compositions of this invention can be used in a wide range of packaging
16 materials, and are not restricted to flexible packaging films and articles such
17 as pouches produced from such films. The compositions may also be used in
18 the preparation of rigid and semi rigid packaging materials. Typical rigid and
19 semi rigid articles include plastic, paper or cardboard cartons, bottles such as
20 juice containers, thermoformed trays, or cups with wall thicknesses of about
21 100 to 2000 microns. The walls of such articles comprise single or multiple
22 layers of materials. The compositions can be used as the sole polymeric
23 material from which one or more layers of a film are formed (i.e., the film can
24 be a multilayer film having, for example, a gas barrier layer, a seal layer, etc.),
25 it can be blended with other polymeric oxygen scavenging agents (such as
26 polybutadiene) or it can be blended with one or more diluent polymers which
27 are known to be useful in the formation of packaging film materials and which
28 often can render the resultant film more flexible and/or processable. Suitable
29 diluent polymers include, but are not limited to, polyethylene such as, for
30 example, low density polyethylene, very low density polyethylene, ultra-low

1 density polyethylene, high density polyethylene, and linear low density
2 polyethylene; polyesters such as, for example, polyethylene terephthalate
3 (PET); polyvinyl chloride (PVC); polyvinylidene chloride (PVDC); and ethylene
4 copolymers such as ethylene/vinyl acetate copolymer, ethylene/alkyl
5 (meth)acrylate copolymers, ethylene/(meth)acrylic acid copolymers, and
6 ionomers. Blends of different diluent polymers also can be used.

7
8 The compositions of this invention can also be used in non integral packaging
9 components such as coatings, bottle cap liners, adhesive and non adhesive
10 sheet inserts, coupons, gaskets, sealants or fibrous mass inserts.

11
12 Generally, the foregoing diluent polymers are semi-crystalline materials.
13 Advantageously, the polymeric component of the composition of the present
14 invention can be crystalline or semi-crystalline at ambient conditions and,
15 accordingly, can be especially compatible with such diluent polymers.
16 Selection of a particular diluent polymer(s) depends largely on the article to
17 be manufactured and the end use thereof. For instance, certain polymers are
18 known by the ordinarily skilled artisan to provide clarity, cleanliness, barrier
19 properties, mechanical properties, and/or texture to the resultant article.

20
21 In combination with the polymeric component, the oxygen scavenging
22 composition of the present invention includes a transition metal compound as
23 an oxygen scavenger catalyst. The transition metal catalyst can be a salt
24 which includes a metal selected from the first, second, or third transition
25 series of the Periodic Table. The metal preferably is Rh, Ru, or one of the
26 elements in the series of Sc to Zn (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and
27 Zn), more preferably at least one of Mn, Fe, Co, Ni, and Cu, and most
28 preferably Co. Suitable anions for such salts include, but are not limited to,
29 chloride, acetate, oleate, stearate, palmitate, 2-ethylhexanoate,
30 neodecanoate, and naphthenate. Representative salts include cobalt (II)

1 2-ethylhexanoate, cobalt oleate, and cobalt (II) neodecanoate. (The metal
2 salt also can be an ionomer, in which case a polymeric counterion is
3 employed.)
4

5 When used in forming a packaging article, the oxygen scavenging
6 composition of the present invention can include only the above-described
7 polymers and a transition metal catalyst. However, photoinitiators can be
8 added to further facilitate and control the initiation of oxygen scavenging
9 properties. Adding a photoinitiator or a blend of photoinitiators to the oxygen
10 scavenging composition can be preferred, especially where antioxidants have
11 been added to prevent premature oxidation of the composition during
12 processing and storage.
13

14 Suitable photoinitiators are known to those skilled in the art. See, e.g., PCT
15 Publication WO 97/07161, WO 97/44364, WO 98/51758, and WO 98/51759,
16 the teachings of which are incorporated herein by reference as if set forth in
17 full. Specific examples of suitable photoinitiators include, but are not limited
18 to, benzophenone, and its derivatives, such as methoxybenzophenone,
19 dimethoxybenzophenone, dimethylbenzophenone, diphenoxybenzophenone,
20 allyloxybenzophenone, diallyloxybenzophenone, dodecyloxybenzophenone,
21 dibenzosuberone, 4,4'-bis(4-isopropylphenoxy)benzophenone,
22 4-morpholinobenzophenone, 4-aminobenzophenone, tribenzoyl
23 triphenylbenzene, tritoluoyl triphenylbenzene, 4,4'-bis(dimethylamino)-
24 benzophenone, acetophenone and its derivatives, such as, o-methoxy-
25 acetophenone, 4'-methoxyacetophenone, valerophenone, hexanophenone,
26 α -phenyl-butyrophenone, p-morpholinopropiophenone, benzoin and its
27 derivatives, such as, benzoin methyl ether, benzoin butyl ether, benzoin
28 tetrahydropyranyl ether, 4-o-morpholinodeoxybenzoin, substituted and
29 unsubstituted anthraquinones, α -tetralone, acenaphthenequinone,
30 9-acetylphenanthrene, 2-acetyl-phenanthrene, 10-thioxanthenone, 3-acetyl-

1 phenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone,
2 1,3,5-triacetylbenzene, thioxanthen-9-one, isopropylthioxanthen-9-one,
3 xanthene-9-one, 7-H-benz[de]anthracen-7-one, 1'-acetonaphthone,
4 2'-acetonaphthone, acetonaphthone, benz[de]anthracen-7-one,
5 1'-acetonaphthone, 2'-acetonaphthone, acetonaphthone, benz[a]anthracene-
6 7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,
7 α,α -diethoxyacetophenone, α,α -dibutoxyacetophenone, 4-benzoyl-4'-
8 methyl(diphenyl sulfide) and the like. Single oxygen-generating
9 photosensitizers such as Rose Bengal, methylene blue, and
10 tetraphenylporphine as well as polymeric initiators such as poly(ethylene
11 carbon monoxide) and oligo[2-hydroxy-2-methyl-1-[4-(1-
12 methylvinyl)phenyl]propanone] also can be used. However, photoinitiators
13 are preferred because they generally provide faster and more efficient
14 initiation. When actinic radiation is used, photoinitiators can provide initiation
15 at longer wavelengths which are less costly to generate and present less
16 harmful side effects than shorter wavelengths.

17

18 When a photoinitiator is present, it can enhance and/or facilitate the initiation
19 of oxygen scavenging by the composition of the present invention upon
20 exposure to radiation. The amount of photoinitiator can depend on the
21 amount and type of cyclic unsaturation present in the polymer, the
22 wavelength and intensity of radiation used, the nature and amount of
23 antioxidants used, and the type of photoinitiator used. The amount of
24 photoinitiator also can depend on how the scavenging composition is used.
25 For instance, if a photoinitiator-containing composition is in a film layer, which
26 underneath another layer is somewhat opaque to the radiation used, more
27 initiator might be needed. However, the amount of photoinitiator used for
28 most applications ranges from about 0.01 to about 10% (By wt.) of the total
29 composition. Oxygen scavenging can be initiated by exposing an article

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1 containing the composition of the present invention to actinic or electron
2 beam radiation, as described below.

3
4 One or more antioxidants can be incorporated into the scavenging
5 composition of the present invention to retard degradation of the components
6 during compounding and film formation. Although such additives prolong the
7 induction period for oxygen scavenging activity to occur in the absence of
8 irradiation, the layer or article (and any incorporated photoinitiator) can be
9 exposed to radiation at the time oxygen scavenging properties are required.
10 Suitable antioxidants include 2,6-di(t-butyl)-4-methylphenol(BHT),
11 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite, tris-
12 (nonylphenyl)phosphite, dilaurylthiodipropionate, vitamin E (α -tocopherol),
13 octadecyl 3,5,-di-tert-butyl-4-hydroxyhydrocinnamate,
14 tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane and
15 the like.

16
17 When an antioxidant is included as part of the composition of the present
18 invention, it preferably is present in an amount which prevents oxidation of the
19 components of the oxygen scavenging composition as well as other materials
20 present in a resultant blend during formation and processing; however, the
21 amount preferably is less than that which interferes with the scavenging
22 activity of the resultant layer, film, or article after initiation has occurred. The
23 amount needed in a given composition can depend on the components
24 present therein, the particular antioxidant used, the degree and amount of
25 thermal processing used to form the shaped article, and the dosage and
26 wavelength of radiation applied to initiate oxygen scavenging. Typically, such
27 antioxidant(s) are used in an amount of from about 0.01 to about 1% (by wt.).
28
29 Other additives that also can be included in the oxygen scavenging
30 composition of the present invention include, but are not necessarily limited

1 to, fillers, pigments, dyestuffs, processing aids, plasticizers, antifog agents,
2 antiblocking agents, and the like.

3

4 The amounts of the components used in the oxygen scavenging composition
5 of the present invention can affect the use and effectiveness of this
6 composition. Thus, the amounts of polymer, transition metal catalyst, and
7 any photoinitiator, antioxidant, polymeric diluents, additives, etc., can vary
8 depending on the desired article and its end use. For example, one of the
9 primary functions of the polymer described above is to react irreversibly with
10 oxygen during the scavenging process, while a primary function of the
11 transition metal catalyst is to facilitate this process. Thus, to a large extent,
12 the amount of polymer present affects the oxygen scavenging capacity of the
13 composition, i.e., the amount of oxygen that the composition can consume,
14 while the amount of transition metal catalyst affects the rate at which oxygen
15 is consumed as well as the induction period.

16

17 The composition of the present invention can provide oxygen scavenging
18 properties at a desirable rate and capacity while having good processing and
19 compatibility properties relative to compositions including conventional non-
20 cyclic ethylenically unsaturated polymers. Thus, the present composition can
21 be used to provide, by itself or as a blend with diluent film-forming polymers
22 such as polyolefins and the like, a packaging material or film that can be
23 manufactured and processed easily. Further, the subject oxygen scavenging
24 composition will deplete the oxygen within a package cavity without
25 substantially detracting from the color, taste, and/or odor of the product
26 contained therein.

27

28 The amount of the polymeric scavenging component contained in the subject
29 composition can range from about 1 to almost about 100%, preferably from
30 about 5 to about 97.5%, more preferably from about 10 to 95%, even more

1 preferably from about 15 to about 92.5%, still more preferably from about 20
2 to about 90%, (with all the foregoing percentages being by weight) of the
3 composition or layer made therefrom. Typically, the amount of transition
4 metal catalyst can range from 0.001 to 1% (by wt.) of the scavenging
5 composition, based on the metal content only (i.e., excluding ligands,
6 counterions, etc.). Where one or more other scavenging compounds and/or
7 diluent polymers are used as part of the composition, such other materials
8 can make up as much as 99%, preferably up to about 75%, by weight of the
9 scavenging composition. Any further additives employed normally do not
10 make up more than 10%, preferably no more than about 5%, by weight of the
11 scavenging composition.

12

13 As indicated above, the composition of the present invention can be used to
14 produce a scavenging monolayer film, a scavenging layer of a multilayer film,
15 or other articles for a variety of packaging applications. Single layer articles
16 can be prepared readily by extrusion processing. Multilayer films typically are
17 prepared using coextrusion, coating, lamination or processing. Multilayer
18 films typically are prepared using coextrusion, coating, lamination or
19 extrusion/lamination as taught in, for example, U.S. Patents 5,350,622 and
20 5,529,833, the teachings of which are incorporated herein by reference as if
21 set forth in full. At least one of the additional layers of multilayer article can
22 include a material having a permeance to oxygen of no more than about
23 $5.8 \times 10^{-8} \text{ cm}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$ (i.e., about $500 \text{ cm}^3/\text{m}^2 \cdot 24 \text{ hours} \cdot \text{atm}$) at about 25°C.
24 Polymers which are commonly used in such oxygen barrier layers include
25 poly(ethylene/vinyl alcohol), poly(vinyl alcohol), polyacrylonitrile, PVC, PVDC,
26 PET, silica, and polyamides such as nylon 6, MXD6, nylon 66, as well as
27 various amide copolymers. (Metal foil layers can also provide oxygen barrier
28 properties.) Other additional layers can include one or more layers which are
29 permeable to oxygen. In one preferred packaging construction, especially
30 flexible packages for food, the layers can include (in order starting from the

1 outside of the package to the innermost layer of the package) (a) an oxygen
2 barrier layer, (b) a scavenging layer, i.e. one that includes the scavenging
3 composition described supra, and optionally, (c) an oxygen permeable layer.
4 Control of the oxygen barrier property of layer (a) provides a means to
5 regulate the scavenging life of the package by limiting the rate of oxygen
6 entry to the scavenging layer (b), thus limiting the rate of consumption of
7 scavenging capacity. Control of the oxygen permeability of layer (c) provides
8 a means to set an upper limit on the rate of oxygen scavenging for the overall
9 structure independent of the composition of scavenging layer (b). This can
10 serve the purpose of extending the handling lifetime of the film in the
11 presence of air prior to sealing of the package. Furthermore, layer (c) can
12 provide a barrier to migration of the individual components or byproducts of
13 the scavenging layer into the package interior. The term "exposed to the
14 interior" refers to a portion of a packaging article having the subject
15 scavenging composition which is either directly exposed or indirectly exposed
16 (via layers which are O₂ permeable) to the interior cavity having oxygen
17 sensitive product. Even further, layer (c) also can improve the heat
18 sealability, clarity, and/or resistance to blocking of the multilayer film. Further
19 additional layers such as the layers, easy open layers, and seal layers can
20 also be used. Polymers typically used in such tie layers include, for example,
21 anhydride functional polyolefins.
22
23 The method of the present invention includes exposing the above-described
24 composition to a package cavity having an oxygen sensitive product therein.
25 A preferred embodiment provides for including a photoinitiator as part of the
26 subject composition and subjecting a film, layer, or article that includes such a
27 composition to radiation so as to initiate oxygen scavenging at desired rates.
28 The thermal radiation used in heating and processing polymers typically used
29 in packaging films (e.g., 100-250°C) advantageously does not trigger the
30 oxygen scavenging reaction.

1
2 The initiating radiation preferably is actinic, e.g., UV or visible light having a
3 wavelength of from about 200 to about 750 nm, preferably of from about 200
4 to 600 nm, and most preferably from about 200 to 400 nm. Such light can be
5 delivered in a continuous or pulsed manner. The layer, film, etc., containing
6 the oxygen scavenging composition preferably is exposed to such radiation
7 until it receives at least about 1 J/g of radiation, more preferably until it
8 receives a dose in the range of about 10 to about 2000 J/g. The radiation
9 also can be electron-beam radiation at a dosage of at least about 2 kiloGray
10 (kG), preferably from about 10 to about 100 kG. Other potential sources of
11 radiation include ionizing radiation such as gamma, X-ray, and corona
12 discharge. Duration of exposure depends on several factors including, but
13 not limited to, the amount and type of photoinitiator present, thickness of the
14 layers to be exposed, thickness and opacity of intervening layers, amount of
15 any antioxidant present, and the wavelength and intensity of the radiation
16 source.

17
18 When using oxygen scavenging layers or articles, irradiation can occur during
19 or after the layer or article is prepared. If the resulting layer or articles is to be
20 used to package an oxygen sensitive product, exposure can be just prior to,
21 during, or after packaging. For best uniformity of radiation, exposure
22 preferably occurs at a processing stage where the layer or article is in the
23 form of a flat sheet. For further information on initiation via irradiation, the
24 reader is directed to PCT publications WO 98/05555 and WO 98/05703, as
25 well as PCT 97/13598, 97/13370, 97/13369, the teachings of which are
26 incorporated herein by reference.

27
28 Determining the oxygen scavenging rate and capacity of a given oxygen
29 scavenging composition contemplated for a particular use can be beneficial.
30 To determine the rate, the time elapsed before the scavenger depletes a

1 certain amount of oxygen from a sealed container is measured. In some
2 instances, the rate can be determined adequately by placing a film containing
3 the desired scavenging composition in an air-tight, sealed container of an
4 oxygen containing atmosphere, e.g., air which typically contains 20.6% (by
5 vol.) O₂. Over time, samples of the atmosphere inside the container are
6 removed to determine the percentage of oxygen remaining. (Usually, the
7 specific rates obtained vary under different temperature and atmospheric
8 conditions. Atmospheres having lower initial oxygen content and/or
9 maintained under low temperature conditions provide a more stringent test of
10 the scavenging ability and rate of a composition. The rates which follow are
11 at room temperature and one atmosphere of air, unless otherwise specified.)
12 When an active oxygen barrier is needed, a useful scavenging rate can be as
13 low as about 0.05 cm³ oxygen per gram of the polymer in the scavenging
14 composition per day in air at 25°C and at 1 atm (101.3 kPa). However, in
15 most instances, the present composition has a rate equal to or greater than
16 about 5.8×10^{-8} cm³/g•s (0.5 cm³/g•day), even up to or greater than about
17 5.8×10^{-5} cm³/g•s (5 cm³/g•day). Further, films or layers including the subject
18 composition are capable of a scavenging rate greater than about
19 1.2×10^{-4} cm³/m²•s (10 cm³/m²•day) and under some conditions, greater than
20 about 2.9×10^{-4} cm³/m²•s (25 cm³/m²•day). (Generally, films or layers
21 generally deemed suitable for use as an active oxygen barrier can have a
22 scavenging rate as low as 1.2×10^{-5} cm³/m²•s (1 cm³/m²•day) when measured
23 in air at 25°C and 101 kPa (1 atm). Such rates make those layers suitable for
24 scavenging oxygen from within a package, as well as suitable for active
25 oxygen barrier applications.

26
27 When the method of the present invention is to be used in an active oxygen
28 barrier application, the initiated oxygen scavenging activity, in combination
29 with any oxygen barriers, preferably creates an overall oxygen permeance of
30 less than about 1.1×10^{-10} cm³/m²•s•Pa (1.0 cm³/m²•day•atm) at 25°C. The

1 oxygen scavenging capacity preferably is such that this value is not exceeded
2 for at least two days.

3

4 Once scavenging has been initiated, the scavenging composition, layer, or
5 article prepared therefrom preferably is able to scavenge up to its capacity,
6 i.e., the amount of oxygen which the scavenger is capable of consuming
7 before it becomes ineffective. In actual use, the capacity required for a given
8 application can depend on the quantity of oxygen initially present in the
9 package, the rate of oxygen entry into the package in the absence of the
10 scavenging property, and the intended shelf life for the package. When using
11 scavengers that include the composition of the present invention, the capacity
12 can be as low as 1 cm³/g, but can be 50 cm³/g or higher. When such
13 scavengers are in a layer of a film, the layer preferably has an oxygen
14 capacity of at least about 9.8 cm³/m² per μm thickness (1200 cm³/m² per mil).

15

16 The composition of the present invention has been found to be capable of
17 providing a film, layer or article which substantially retains its physical
18 properties (e.g., tensile strength and modulus) even after substantial oxygen
19 scavenging has occurred. In addition, the present composition does not
20 provide significant amounts of byproducts and/or effluents, which can impart
21 an undesired taste, color, and/or odor to the packaged product.

22

23 This invention relates to an oxygen scavenging polymer composition
24 comprising cyclic allylic pendent groups which can be used in oxygen
25 scavenging packaging material which have either no or low volatile oxidation
26 by-products. Minimizing volatile by-products reduces the problem of
27 organoleptics in oxygen scavenging food packaging.

28 The polymer composition with cyclic allylic pendent groups can be made by
29 grafting methyl cyclohex-1-ene-4-methanol, cyclohex-1-ene-4-methanol

1 (1,2,5,6-tetrahydrobenzyl alcohol) and cyclohex-1-ene-4-propanol onto EMAC
2 resins by transesterification of the corresponding alcohols or transamidation
3 of the corresponding amines with the methyl esters on EMAC to give modified
4 EMAC having pendent cyclic olefins (see Figure 1). The composition can
5 also be made by direct polymerization.

6 The esterification, transesterification, amidation or transamidation reaction
7 can be a solution reaction or by reactive extrusion. The catalysts can be any
8 one of strong non-oxidizing acids, tertiary amines, Group I alkoxides,
9 Group IVB alkoxides and Group IVA metal organics. The level of olefin in the
10 final products can be controlled by the level of transesterification and the
11 methyl ester content of the start EMAC. The molecular weight of the
12 polymers largely depends on the molecular weight of the EMAC feeds.

13 In a preferred embodiment, these products are combined with a transition-
14 metal salt to catalyze the oxygen scavenging properties of the materials. A
15 transition-metal salt, as the term is used here, comprises an element chosen
16 from the first, second and third transition series of the periodic table of the
17 elements, particularly one that is capable of promoting oxidation reactions.
18 This transition-metal salt is in a form which facilitates or imparts scavenging of
19 oxygen by the composition of this invention. A plausible mechanism, not
20 intended to place limitations on this invention, is that the transition element
21 can readily inter-convert between at least two oxidation states and facilitates
22 formation of free radicals. Suitable transition-metal elements include, but are
23 not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III,
24 copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the
25 transition-metal element when introduced into the composition is not
26 necessarily that of the active form. It is only necessary to have the transition-
27 metal element in its active form at or shortly before the time that the
28 composition is required to scavenge oxygen. The transition-metal element is

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1 preferably iron, nickel or copper, more preferably manganese and most
2 preferably cobalt.

3 Suitable counter-ions for the transition metal element are organic or inorganic
4 anions. These include, but are not limited to, chloride, acetate, stearate,
5 oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate,
6 neodecanoate or naphthenate. Organic anions are preferred. Particularly
7 preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt
8 stearate, cobalt oleate and cobalt neodecanoate. The transition-metal
9 element may also be introduced as an ionomer, in which case a polymeric
10 counter-ion is employed.

11 The composition of the present invention when used in forming a oxygen
12 scavenging packaging article can be composed solely of the above described
13 polymer and transition metal catalyst. However, components, such as
14 photoinitiators, can be added to further facilitate and control the initiation of
15 oxygen scavenging properties. For instance, it is often preferable to add a
16 photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger
17 compositions, especially when antioxidants are included to prevent premature
18 oxidation of that composition during processing.

19 Suitable photoinitiators are well known in the art. Such photoinitiators are
20 discussed in U.S. Patent No. 5,211,875. It is also discussed In U.S. Patent
21 Application Serial No. 08/857,325, in which some of the present inventors
22 were contributing inventors and which is incorporated herein by reference.
23 Specific examples include, but are not limited to, benzophenone, o-methoxy-
24 benzophenone, acetophenone, o-methoxy-acetophenone,
25 acenaphthenequinone, methyl ethyl ketone, valerophenone, hexanophenone,
26 α -phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone,
27 4-morpholinobenzophenone, benzoin, benzoin methyl ether,
28 4-o-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone,

1 4'-methoxyacetophenone, substituted and unsubstituted anthraquinones,
2 α -tetralone, 9-acetylphenanthrene, 2-acetyl-phenanthrene,
3 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole, 9-fluorenone,
4 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one,
5 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl ether,
6 4,4'-bis(dimethylamino)-benzophenone, 1'-acetonaphthone,
7 2'-acetonaphthone, acetonaphthone and 2,3-butanedione,
8 benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,
9 α,α -diethoxy-acetophenone, α,α -dibutoxyacetophenone, etc. Singlet oxygen
10 generating photosensitizers such as Rose Bengal, methylene blue, and
11 tetraphenyl porphine may also be employed as photoinitiators. Polymeric
12 initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-
13 methyl-1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is
14 preferable because it generally provides faster and more efficient initiation.

15 When a photoinitiator is used, its primary function is to enhance and facilitate
16 the initiation of oxygen scavenging upon exposure to radiation. The amount
17 of photoinitiator can vary. In many instances, the amount will depend on the
18 amount and type of oxygen scavenging polymer in the present invention, the
19 wavelength and intensity of radiation used, the nature and amount of
20 antioxidants used, as well as the type of photoinitiator used. The amount of
21 photoinitiator also depends on how the scavenging composition is used. For
22 instance, if the photoinitiator-coating composition is placed underneath a layer
23 which is somewhat opaque to the radiation used, more initiator may be
24 needed. For most purposes, however, the amount of photoinitiator, when
25 used, will be in the range of 0.01 to 10% by weight of the total composition.
26 The initiating of oxygen scavenging can be accomplished by exposing the
27 packaging article to actinic or electron beam radiation, as described below.

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1 Antioxidants may be incorporated into the scavenging compositions of this
2 invention to control degradation of the components during compounding and
3 shaping. An antioxidant, as defined herein, is any material which inhibits
4 oxidative degradation or cross-linking of polymers. Typically, such
5 antioxidants are added to facilitate the processing of polymeric materials
6 and/or prolong their useful shelf-life.

7 Antioxidants such as Vitamin E, Irganox® 1010, Irganox® 1076,
8 2,6-di(t-butyl)-4-methyl-phenol(BHT), 2,6-di(t-butyl)-4-ethyl-phenol (BHEB),
9 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite,
10 tris-(nonylphenyl)phosphite and dilaurylthlodipropionate would be suitable for
11 use with this invention.

12 When an antioxidant is included as part of the present composition, it should
13 be used in amounts which will prevent oxidation of the scavenger
14 composition's components as well as other materials present in a resultant
15 blend during formation and processing but the amount should be less than
16 that which would interfere with the scavenging activity of the resultant layer,
17 film or article. The particular amount needed will depend on the particular
18 components of the composition, the particular antioxidant used, the degree
19 and amount of thermal processing used to form the shaped article, and the
20 dosage and wavelength of radiation applied to initiate oxygen scavenging and
21 can be determined by conventional means. Typically, they are present in
22 about 0.01 to 1% by weight.

23 Other additives which may also be included in oxygen scavenger layers
24 include, but are not necessarily limited to, fillers, pigments, dyestuffs,
25 stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

26 The amounts of the components which are used in the oxygen scavenging
27 compositions, or layers have an effect on the use, effectiveness and results of